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PROCEEDINGS OF THE SECOND ISOTOPE SEPARATION WORKSHOP

Research Report No 88-99-K

H.D. Morrison and J.A. O'Neill
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ABSTRACT

The Second Isotope Separation Workshop was held June 13 and 14, 1985 at Ontario Hydro's Conference and Development Centre in Orangeville. Researchers from AECL (Chalk River), Lumonics Inc., the National Research Council, the Universities of McMaster, Montreal, Toronto and Waterloo, and Ontario Hydro met to discuss progress in isotope separation. In particular, methods for separating zirconium-91, carbon-14, lithium-6 and uranium-235 were presented. Many of the methods are technically feasible and several appear to be commercially viable.

job	file	date	report no.
16-590	819.312	April 25, 1988	88-99-K

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EXECUTIVE SUMMARY

PROCEEDINGS OF THE SECOND ISOTOPE SEPARATION WORKSHOP

H.D. Morrison and J.A. O'Neill

The Second Isotope Separation Workshop is the successor to the Zirconium Isotope Separation Workshop held in 1984 at Orangeville. At the first Workshop, our attention was concentrated on the benefits of zirconium-91 depleted zirconium for CANDU reactors, and on methods for producing such material. While there is a continuing interest in zirconium separation, there is also interest in separating isotopes of other elements for which commercial markets exist. Thus, the scope of the Second Workshop was expanded beyond zirconium to discuss isotope separation in general.

The Workshop was divided into two sessions. The first session examined the present role of Ontario Hydro in isotope separation, in particular at Research Division and through the Isotope Sales and Services Program, and examined future commercial opportunities for isotopes. One of the concepts for future opportunities is isotopic tailoring for materials employed in the fission power market and future fusion power market. Depletion of zirconium in zirconium-91 falls into this category, as does the removal from stainless steel of nitrogen-14, a precursor of carbon-14.

The second session was devoted to techniques for separating isotopes including presentations on separating carbon-14, uranium-235, lithium-6, deuterium and tritium. Of special interest were two invited presentations, one from TRW on developments in their Plasma Separation Process, and the other from Westinghouse on the progress and status of their zirconium separation program. The TRW Plasma Separation Process is a general purpose method, already demonstrated on 20% of the elements in the periodic table. The Westinghouse zirconium program, before its termination in 1985 due to funding restraints, demonstrated the technical feasibility of three processes. One of the three, solvent extraction, is economically viable for fuel cladding. Thus, it is certainly economic for pressure tubes in CANDU reactors.

There are few forums for topical discussion of isotope separation other than this series of Workshops organized by Ontario Hydro. Given the high level of interest demonstrated at this Workshop in continuing research and development of isotope separation techniques, a third Workshop should be held to review progress and interest in this field.

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To

Dr. D. Mills
Director of Research

PROCEEDINGS OF THE SECOND ISOTOPE SEPARATION WORKSHOP

1.0 INTRODUCTION

In 1984, Ontario Hydro organized a meeting of scientists and engineers interested in zirconium isotope separation. That meeting, known as the Zirconium Isotope Separation Workshop, attracted 25 people from industry and universities to hear 9 presentations devoted to the benefits and methods of separating isotopes of zirconium /1/. Encouraged by the enthusiastic response to this first meeting, a second meeting was planned for the following year to review progress in isotope separation for any element for which commercial markets exist. With the expanded scope came a change in name. Thus, the Second Isotope Separation Workshop was held at Ontario Hydro's Conference and Development Centre in Orangeville, June 13 and 14, 1985.

The Workshop was attended by 36 people drawn from AECL, Lumonics Inc., NRC, McMaster University, University of Montreal, University of Toronto, University of Waterloo, and Ontario Hydro. In addition, there were two invited speakers: Steven Suchard from TRW in California, and Ed Lahoda from Westinghouse in Pennsylvania. Fifteen presentations were given in two sessions. The first session examined present and future trends in isotope separation with respect to the benefits for industry and medicine. The second session concentrated on techniques for separating isotopes, including four papers on zirconium, and one each on carbon, lithium, uranium and hydrogen.

The program of the meeting, listing the contributors and the titles of their presentations, appears as Appendix A. Summaries of most of the presentations, together with copies of the overheads where available, make up Appendix B. An overview of all the presentations follows here to guide those who did not attend the Workshop.

2.0 WORKSHOP I: BACKGROUND

The first session began with an introduction and welcome by Mr. A.F. Baljet, Manager of the Electrical Research Department in Ontario Hydro Research Division. Most of the isotope separation work at Ontario Hydro is performed within the Electrical Research Department. Mr. Baljet discussed the importance of isotope separation to Ontario Hydro in support of its nuclear power program and the benefits of continuing research.

The second presentation was an overview of Ontario Hydro's Isotope Sales and Services Program presented by Mr. J.W. Richman. This Program handles sales of heavy water, produced by our Bruce Heavy Water plant, and of cobalt-60, and provides services related to upgrading heavy water. They are planning to market deuterium gas, helium-3, and tritium, the latter two as products of the Tritium Removal Facility at Darlington. In short, the marketing of any isotope needed or produced by Ontario Hydro, and of the expertise in handling such isotopes, lies in the area of the Isotope Sales and Services Program.

The final presentation of the first session was a talk by Dr. J.A. O'Neill on possible future commercial opportunities for isotopes. Three markets were examined: the medical market, the fission power market, and the fusion power market. In medicine, new radioisotopes with fewer side effects and greater specificity are always welcomed. In the two nuclear power markets, the emphasis is on tailoring the containment materials to reduce neutron absorption, as is the case for removing ^{91}Zr, or to remove the precursors of long-lived radioisotopes, such as removing ^{14}N which becomes ^{14}C. Thus, isotopic tailoring could improve operation or could reduce the costs of decommissioning.

3.0 WORKSHOP II: SEPARATION TECHNIQUES

The second session began with an invited talk by Dr. S.N. Suchard from TRW on their Plasma Separation Process. The basis of this technique is selective rf excitation of ions to alter their cyclotron orbits as they drift through a uniform magnetic field. The technique is completely general, and has already been used to separate 20% of the elements in the periodic table. For each element, different methods may be required for producing and collecting the ions, but the separation principle is the same for all. High throughput requires a large volume magnet to minimize collisions between ions because collisions reduce the selectivity.

In the second talk, Dr. E.A. Symons, AECL, reviewed potential methods for separating lithium isotopes. Lithium-6 is of interest for tritium breeding blankets to provide fuel for fusion reactors. Current requirements are being met by stockpiles from the COLEX process operation. Higher demands, estimated from 5 to 300 Mg/a by the middle of the next century, could be met economically by any of four techniques: chemical exchange, displacement chromatography, laser-based systems, and possibly rf spectroscopy. The former two techniques are better developed than the latter two.

Next, Dr. K.B. Woodall, Ontario Hydro Research Division presented a summary of a laser-based system and of cryogenic distillation for separating ^{14}C. This isotope is produced in Ontario Hydro's nuclear reactors at a rate currently 10 times the world demand (it will be 25 times after Darlington is completed). Separation of the ^{14}C would reduce the volume of radioactive waste removed from the nuclear reactors, and could displace the current production obtained by irradiating aluminum nitride. The laser method is based on selective dissociation of formaldehyde to produce carbon monoxide enriched in ^{14}C and hydrogen. Cryogenic distillation requires fewer chemical steps than the laser method because it works directly with carbon monoxide. Both methods are technically feasible and practicable.

Ion exchange chromatography is another example of a technique applicable to many elements and suitable for industrial scale. Dr. K.J. Franklin, AECL, discussed this method with particular reference to the separation of ^{235}U. The Asahi Chemical Exchange Process (ACEP), developed in Japan, has been established as a feasible method for uranium enrichment based on redox ion exchange chromatography. This method is unsuitable for the production of highly enriched uranium because of the long lead time and problems with criticality. The production of low-enriched uranium in Canada, however, is particularly attractive by ACEP.

In the fifth talk, Dr. R.D. McAlpine, AECL, examined factors in the selection of working molecules for laser isotope separation by multiphoton decomposition. Most of the examples applied to separating hydrogen isotopes. A thorough list of factors for assessing working molecules were presented in the context of the four processes involved in this laser method:

chemical exchange from the isotope source to the working molecule, laser decomposition of the working molecule into secondary species, capture of the secondary species, and transformation of the secondary species into a usable product.

The first half of this session concluded with a presentation by Dr. G.F. Thomas, Ontario Hydro Research Division, on some theoretical aspects of multiphoton excitation. In particular, he described the effects of electrical anharmonicity on the coherent multiphoton excitation of a molecule by a laser in the presence of a dc field. The theory explains the observed enhancement in the infrared multiphoton dissociation of CF_3D in the presence of a static field.

The second half of this session opened with an invited talk by Dr. E.J. Lahoda of Westinghouse reviewing their efforts in zirconium separation. The motivation lay in improving the efficiency of fission fuel bundles by reducing the neutron absorption in the zirconium fuel cladding. For this purpose, the added cost of zirconium separation must be on the order of $100/kg or less. The Westinghouse program examined three methods: molecular isotope separation by laser, photo-assisted solvent extraction, and solvent extraction. Of the three, solvent extraction is the cheapest and is the only one that is economically viable. Soon after technical feasibility was demonstrated in March 1985, the entire program was terminated due to general tightness of funds in Westinghouse's Nuclear Fuels Division.

The next talk, given by Dr. T.E. Gough, University of Waterloo, examined progress in separation of ^{91}Zr by collisionless infrared multiphoton dissociation of organozirconium molecules. Two technical challenges successfully overcome in this work are the synthesis of organozirconium molecules and the construction of the molecular beam machine. Most molecules do not work because they are not stable. From the few that do work, the process demonstrates poor prospects for commercial application because the compounds are still difficult to handle and their vapour pressures are too low to be economic.

In the first of two papers from the National Research Council on zirconium separation, Dr. P.A. Hackett summarized experiments on atomic vapour laser isotope separation (AVLIS) for zirconium. The scientific feasibility of zirconium AVLIS has been established. Experiments to put limits on this feasibility are continuing. The principal issue at stake is whether the momentum developed in launching this investigation will continue. In the absence of strong commitment from parties interested in zirconium separation in general and to zirconium AVLIS in particular, time, and perhaps a window of opportunity, will be lost.

The following paper, presented by Dr. O.L. Bourne, NRC, studied modeling of zirconium AVLIS. The atomic beam sources employed in the experiments to resolve the atomic spectra of zirconium may not represent a typical source for a large scale separation process. To generate spectra for such a source, a simple model has been developed that incorporates Doppler broadening and quenching of the excited states. Typical spectra demonstrate selective excitation of ^{91}Zr is possible even at temperatures above 1000 K.

A novel type of light-based isotope separation was presented by Dr. J.W. Hepburn, University of Waterloo. He examined the possibility of exploiting vacuum ultraviolet (VUV) absorption for selective single photon decomposition of molecules. The first problem, obtaining a tunable coherent source of VUV radiation, was solved by four-wave mixing the output of two dye lasers, one tunable, in Mg vapour. With this VUV source, he investigated the photolysis of car-

bon dioxide for separating ^{14}C. A significant isotope shift, observed between $^{12}CO_2$ and $^{13}CO_2$, dispels the notion that all VUV absorption bands are structureless, and supports the scientific feasibility of this method.

4.0 FUTURE WORKSHOPS

To conclude the day's session, and the Workshop, Dr. N. Anyas-Weiss summarized the presentations on separation techniques. Then he led an open discussion on the merits of this type of meeting and on the interest in future meetings. Most attendees felt that the meeting was useful and should be held again. Others expressed an interest in seeing an isotope separation meeting sponsored by Ontario Hydro as part of one of the larger conferences run by any of the scientific societies. Given the level of interest expressed at this meeting and in later correspondence, a third workshop should be held.

5.0 ACKNOWLEDGMENTS

It is a pleasure to thank all those who attended the Second Isotope Separation Workshop, and especially to those who contributed presentations of their work and provided the material for Appendix B.

Approved:

A.F. Baljet
Manager
Electrical Research Department

Submitted:

H.D. Morrison
Physicist
Science Section

J.A. O'Neill
Coordinator, Industrial Laser Program
Divisional Projects Department

REFERENCE

1. J.A. O'Neill, "First Zirconium Isotope Separation Workshop: Summary of Proceedings," Research Report 84-306-K.

APPENDIX A

SECOND ISOTOPE SEPARATION WORKSHOP PROGRAM

Workshop I: Background
Chairman: N. Anyas-Weiss, Ontario Hydro Research Division

1. Introduction and Welcome
   A.F. Baljet, Manager, Electrical Research Department, Research Division, Ontario Hydro

2. Ontario Hydro's Isotope Sales and Services Program
   J.W. Richman, Isotope Sales and Services Program, Design & Development, Ontario Hydro

3. Future Trends in Isotope Separation
   J.A. O'Neill, Ontario Hydro Research Division

Workshop II - Separation Techniques

Part A
Chairman: J.A. O'Neill, Ontario Hydro Research Division

1. The TRW Plasma Process for Isotope Separation
   S.N. Suchard, Energy Division, TRW Space & Technology Group

2. A Review of Potential Methods for Lithium Isotope Separation
   E.A. Symons, AECL, Chalk River

3. Current Status of Carbon Isotope Separation Research at Ontario Hydro
   K.B. Woodall, Ontario Hydro Research Division

4. Isotope Separation by Ion Exchange Chromatography
   K.J. Franklin, AECL, Chalk River

5. Factors in the Selection of Working Molecules for Laser Isotope Separation
   R.D. McAlpine, AECL, Chalk River

6. Electrical Anharmonicity and Coherent Multiphoton Excitation in a Laser + DC Field
   G.F. Thomas, Ontario Hydro Research Division

Part B
Chairman: S.H. Hawthorne, Ontario Hydro Research Division

7. Work at Westinghouse on Zirconium Isotope Separation Technology
   E.J. Lahoda, Westinghouse Research & Development

8. Progress of Waterloo Experiments on CO_2 MPD of Organozirconium Compounds
   T.E. Gough, University of Waterloo

9. Laser Isotope Separation of Zirconium
   P.A. Hackett, NRC, Ottawa

10. Model Studies of Laser Isotope Separation of Zirconium
    O.L. Bourne, NRC, Ottawa

11. Coherent Vacuum Ultraviolet Photochemistry and Isotope Separation
    J.W. Hepburn, University of Waterloo

12. Workshop Summary
    N. Anyas-Weiss, Ontario Hydro Research Division

APPENDIX B

SUMMARY OF PRESENTATIONS

The following pages provide text summaries of the technical presentations and, in most cases, copies of the overheads used. In the cases where no text was available, Dr. H.D. Morrison wrote a summary from notes taken during the sessions. The intention is to provide, as far as possible, a complete record of the Workshop proceedings in the conviction that everyone will benefit from some recall of what was said. Our apologies to the presenters for any incompleteness or inaccuracy in these texts.

FUTURE TRENDS IN ISOTOPE SEPARATION

James A. O'Neill
Electrical Research Department
Ontario Hydro Research Division

In this talk we will look at some of the changes in the demand for isotopes in three separate markets. These markets are the medical market, the nuclear power or fission market, and the future fusion power market.

THE MEDICAL MARKET

The periodic table in Figure 1 shows the major elements essential to human life. For isotopes of Carbon, Nitrogen, Oxygen and Hydrogen there are already large stable markets. There are large scale production techniques in place for isotopes of all these elements, and current supplies are adequate to meet the anticipated demand at the prevailing low prices.

The medical radionuclide market looks different however. The uses of isotopes here are manifold, including medical diagnosis, therapeutic treatments such as radiotherapy, and the use of radionuclide power sources. Figure 2 shows the most important isotopes currently used for diagnostic purposes, and Table 1 gives an indication of the major applications and precursors for these isotopes. Currently, the most profitable radioisotope in this list might be ^{201}Tl. However, the medical diagnosis industry is always on the lookout for new radioisotopes with fewer side effects and greater specificity. This might mean that thallium might be replaced by one of the heavier odd isotopes of calcium which it tries to mimic. Although new isotope separation techniques such as laser based methods might reduce the production costs of the precursors or the radioisotope somewhat, lower prices are not likely to increase the demand sufficiently to warrant this effort for any particular isotope.

THE NUCLEAR FISSION MARKET

Figure 3 lists the isotopes of current importance in the nuclear fission field and the respective areas of application. There are two new areas of opportunity for isotopes in the nuclear field. One of these deals with improved neutron economy and reactor design improvements, while the other area addresses the need for reducing the neutron induced activity in reactor components.

For CANDU-type reactors using zirconium pressure tubes and fuel cladding, about 60% of the neutron absorption is due to ^{91}Zr. The elimination of this isotope from the zirconium used in reactor components or fuel pencils has great economic value. For example, reducing the level of ^{91}Zr to less than 3% from the natural level of 11%, has a value of well over $100/kg for fuel cladding and over $2000/kg for reactor components. The difference in value is largely due to the fact that the fuel cladding remains in the reactor for only about one year. For CANDU reactors world-wide the market for ^{91}Zr-depleted zirconium is over 150 Mg per annum. The light water reactor market would open up if the cost of production for the depleted zirconium fell below $100/kg. A number of potential processes exist to enrich (deplete) selected isotopes of zirconium, so that opportunities exist to tailor the enrichment and hence the cost of the zirconium to meet a particular need.

In Table 2 the major isotopes contributing to gamma and beta activity in fission reactors are shown. During maintenance the main sources of activity are isotopes of cobalt, while during decommissioning nickel and niobium also contribute. The removal of cobalt and niobium from the structural steel and the enrichment of nickel in ^{64}Ni could remove the need for routine shutdowns to decontaminate reactors, and reduce the cost of decommissioning. Assuming that the cost of purifying the iron is about $2/kg, and the enrichment of nickel costs about $1300/kg, the return on this type of investment is about 14% per annum. This type of ROI is reaching the level at which it could become of interest to the nuclear industry. An average PWR or BWR reactor would require about 5 Mg of isotopically tailored material.

THE NUCLEAR FUSION MARKET

Although fusion is not expected to become a commercial reality for several years, it is not too soon to look at the benefits isotopically tailored materials could offer this technology. As with fission power, neutron induced activity reduction would be one of the benefits derived from isotopically tailored structural materials. Another benefit would come from improving the performance of the "first wall". This wall is exposed to the intense high energy neutrons and alpha particles released in the D-T fusion reactions. At the present time it is expected that first wall materials will only last about one year. The large number of atomic displacements and the accumulation of helium will weaken these structures. The removal of ^{54}Fe could double the lifetime of the first wall. A 1000 MW(e) fusion reactor might use between 50 and 500 Mg of steel, depending on design.

Figure 4 shows the dramatic effect the tailoring of 316-stainless steel has on the residual neutron induced activity /1/. This kind of tailoring is particularly useful for fusion reactors, since here all of the activity is neutron induced. By contrast, most of the residual activity in fission reactors is in the spent fuel. Isotopic tailoring for fusion reactors will reduce maintenance costs as well as ultimate disposal costs. It is interesting to note that the reduction of ^{14}N has a dramatic effect on residual activity because of the reduction in ^{14}C. This approach to reactor construction offers a system without the need for long term storage. After a period of less than 100 years, the material can be safely disposed of in a conventional manner.

CONCLUSIONS

In the near future, there are markets for medical radionuclides with a total value ranging in the millions of dollars. Over the next decade, a market for ^{91}Zr could develop which could reach a value of $100 million and more per annum. In the same time frame, a market for enriched ^{64}Ni could also develop. In the more distant future a whole range of isotopically tailored materials predominantly aimed at the fusion power market could be developed.

It is important to remember, that this talk has only dealt with needs which have already been identified. Isotope separation technology has reached the state at which virtually any desired isotope can be selectively enriched or depleted. Therefore, a whole new range of opportunities for improved materials and products can be created.

1. R.W. Conn, K. Okula, and A.W. Johnson, "Minimizing radioactivity and other features of elemental and isotopic tailoring of materials for fusion reactors," Nucl. Technol. 41, 389-400 (1978).

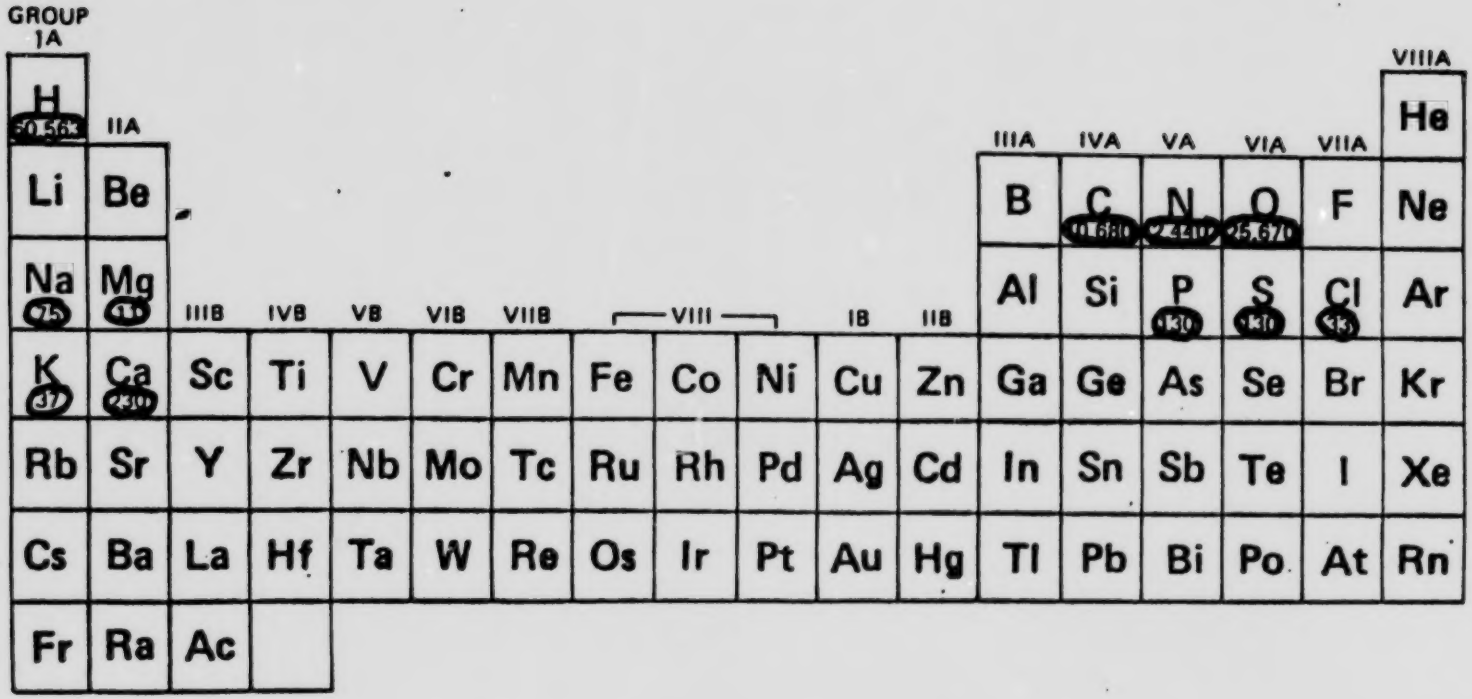


FIGURE 1 - Elements essential to life (numbers indicate abundance of the element in atoms per 100,000 for the human body).

Important Isotopes for Diagnostic Purposes

Projected to have substantial markets:

Technetium-99

Iodine-131 and 123

Thallium-201

Potassium-43

Krypton-81

Calcium-47

FIGURE 2

88-99

TABLE 1

NUCLIDE	USES	PRECURSOR
TECHNETIUM-99	BRAIN, LIVER, LUNG, THYROID, KIDNEY, CEREBRO-SPINAL FLUID SCANS. PLACENTAL LOCALIZATION. CARDIAC FUNCTION ASSESSMENT.	^{98}Mo ^{100}Mo
IODINE-123	THYROID FUNCTION	$^{122,123,126}Te$
IODINE-131	CARDIAC FUNCTION, INTESTINAL ABSORPTION, TUMOUR LOCALIZATION. EXTRA-CELLULAR FLUID VOLUME. PERFUSION STUDIES. THYROID AEROSOL LUNG SCAN. FAT ABSORPTION. KIDNEY FUNCTION, LIVER SCANS.	^{130}Te
THALLIUM-201	CARDIAC FUNCTION. CORONARY ARTERY DISEASE. LOCALIZATION OF INFARCTS.	$^{203,205}Tl$ ^{201}Hg
POTASSIUM-43	MYOCARDIAL SCAN, TUMOUR LOCALIZATION, BLOOD FLOW, RED CELL LABELLING.	^{43}Ca
KRYPTON-81M	LUNG SCANS (AEROSOL). VENTILATION. PERFUSION.	^{79}Br ^{81}Kr
CALCIUM-47	CALCIUM METABOLISM/ABSORPTION BONE TUMOUR DETECTION/ LOCALIZATION.	^{46}Ca

NUCLEAR FISSION FIELD

ISOTOPES CURRENTLY IMPORTANT:

U - ENRICHED FUEL

D - CANDU'S

Li-6 - SLOW NEUTRON SHIELDING

Li-7 - pH ADJUSTMENT

B-10 - CONTROL RODS

FIGURE 3

TABLE 2

INDUCED ACTIVITY REDUCTION

- RADIOACTIVE CRUD

CULPRITS:

MAINTENANCE: ^{58}Co, ^{60}Co

DECOMMISSIONING: ^{60}Co, ^{94}Nb, ^{59}Ni

SOURCES:

$^{58}Ni(n,p)^{58}Co$

$^{58}Ni(n,\gamma)^{59}Ni$

$^{59}Co(n,\gamma)^{60}Co$

$^{62}Ni(n,\gamma)^{63}Ni$

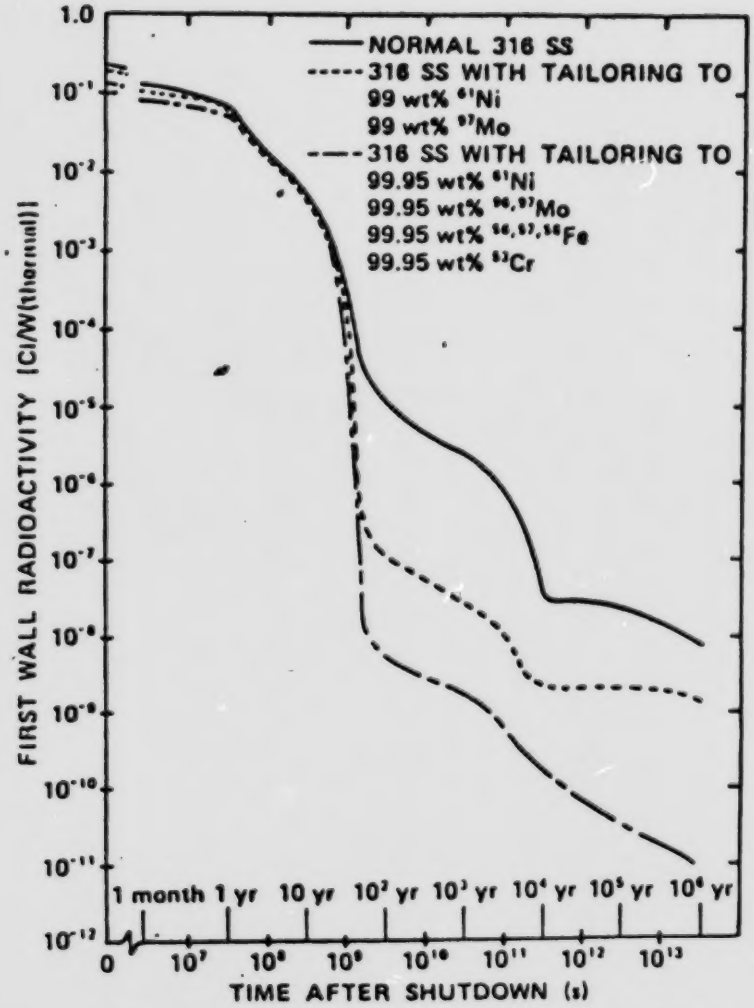
$^{93}Nb(n,\gamma)^{94}Nb$

SOLUTION:

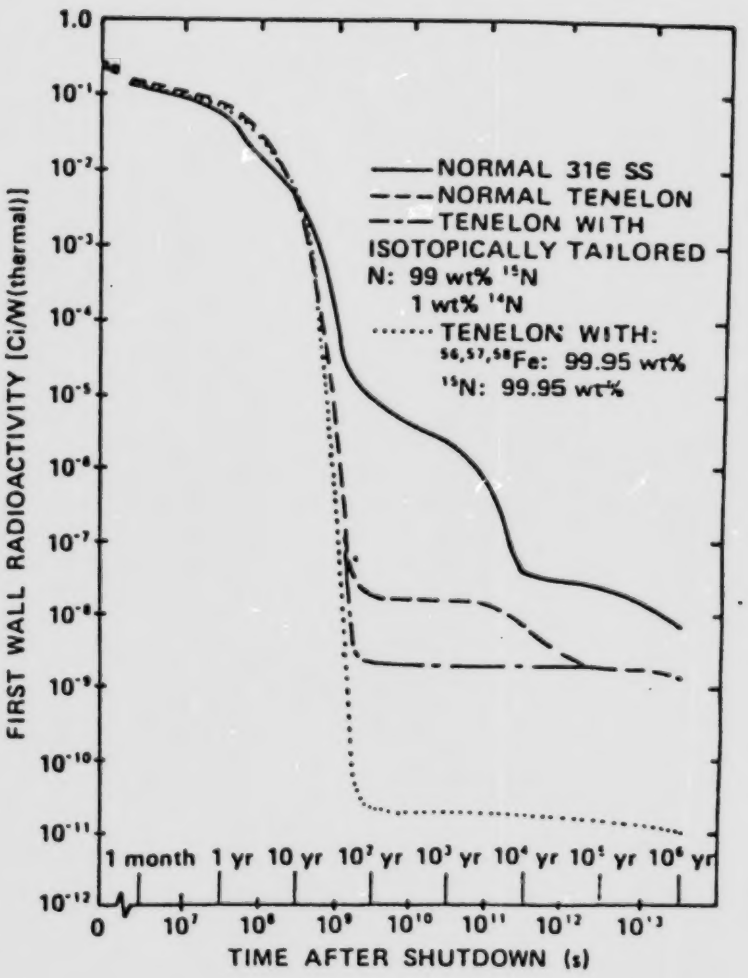
- REMOVE Co, Nb
- ENRICH Ni IN ^{64}Ni

PAYOFF:

- 10 YEAR SHUTDOWNS AVOIDED
- DECOMMISSIONING COSTS REDUCED
- ASSUMING: \$2/Kg FOR Fe PURIFICATION
  \$1300/Kg FOR 99% ^{64}Ni
  R.O.I. = 14%
- DEMAND APPROX 5Mg PER PWR OR BWR


NORMAL 316 SS
316 SS WITH TAILORING TO
99 wt% ^{61}Ni
99 wt% ^{97}Mo
316 SS WITH TAILORING TO
99.95 wt% ^{61}Ni
99.95 wt% ^{96,97}Mo
99.95 wt% ^{56,57,58}Fe
99.95 wt% ^{53}Cr
FIRST WALL RADIOACTIVITY [Ci/W(thermal)]
1 month 1 yr 10 yr 10^2 yr 10^3 yr 10^4 yr 10^5 yr 10^6 yr
TIME AFTER SHUTDOWN (s)

Radioactivity after shutdown for Type 316 stainless-steel first walls isotopically tailored at different selectivity levels: 1.25 MW/m^2 wall loading and 2-yr operation.


NORMAL 316 SS
NORMAL TENELON
TENELON WITH
ISOTOPICALLY TAILORED
N: 99 wt% ^{15}N
1 wt% ^{14}N
TENELON WITH:
^{56,57,58}Fe: 99.95 wt%
^{15}N: 99.95 wt%
FIRST WALL RADIOACTIVITY [Ci/W(thermal)]
1 month 1 yr 10 yr 10^2 yr 10^3 yr 10^4 yr 10^5 yr 10^6 yr
TIME AFTER SHUTDOWN (s)

Radioactivity after shutdown for Tenelon first walls isotopically tailored at different selectivity levels: 1.25 MW/m^2 wall loading and 2-yr operation.

FIGURE 4

THE TRW PLASMA PROCESS FOR ISOTOPE SEPARATION

Steven N. Suchard
Energy Division
TRW Space & Technology Group
One Space Park
Redondo Beach, CA 90278

(Summary by H.D. Morrison, Ontario Hydro Research Division)

The Plasma Separation Process (PSP) was invented by John M. Dawson in 1974 and has been under development at TRW since then /1/. In 1976, PSP became part of the Advanced Isotope Separation Program funded by the Department of Energy. The working material for PSP is a neutral plasma immersed in a uniform magnetic field (e.g. 2 Tesla in a 0.5 m bore superconducting magnet 2 m long). Ions in the plasma move in helical orbits at their ion cyclotron frequency as they drift along the magnetic field lines. The radius of the helix is proportional to the ion's radial velocity and inversely proportional to the ion cyclotron frequency. As the ion cyclotron frequency is proportional to magnetic field strength and inversely proportional to mass, ions of different masses move with different frequencies in different sized orbits. Isotope separation is achieved by exploiting these mass dependent differences.

For example, consider a uranium plasma of singly-charged ions. RF excitation of the plasma at the cyclotron frequency of the ^{235}U ions excites these ions, increasing their velocity and hence their orbital radius. The non-resonant ^{238}U ions remain essentially undisturbed from their smaller initial orbits. The ^{235}U ions are collected on vertical fins, set like blinds at a separation wider than the orbit of the ^{238}U ions. Thus, the ^{235}U ions are scraped out of their larger orbits, while the ^{238}U ions pass between the fins to strike an end plate.

The complete process consists of a plasma source, an RF excitation field within the uniform field of a superconducting magnet, and a collector. About 20% of the elements in the periodic table, including U, Ni, C, N, O, K, In, and Pb have been separated by this method.

The costs of isotope separation with the PSP depend on several material specific and non-specific factors. Factors that affect separation efficiency and material handling are material specific. Separation efficiency depends on the plasma density, collision cross-sections and the hardware configuration (e.g. separation of Hg requires a vertical machine). Material handling chiefly concerns the plasma source and the collector, the technical details of which depend on the chemical and physical properties of the element being separated. For uranium separation, the plasma is produced by sputtering neutral atoms from a solid plate and then ionizing the atoms by collision with electrons excited by microwave radiation. In the collector, the product fins and tails plate are designed for liquid collection.

One cost factor that is non-specific to the material is the product production rate. The important question here is, how much product is needed? The answer will determine the size and number of modules required. At present a 0.5-m module is available at TRW for small scale demonstrations from 1 to 100 g of product. This module has been used to produce 3 g of ^{58}Ni in 48 hours. In tests on uranium, the 0.5-m module enriched the ^{235}U product to 2.25% and

depleted the tails to 0.53%. A production prototype module, 5 m long with a 1 m bore designed for separating quantities over 1 kg, has been constructed. The goal for this module is enrichment of ^{235}U to 3-4%, with less than 0.2% in the tails.

1. J.M. Dawson, H.C. Kim, D. Arnush, B.D. Fried, R.W. Gould, L.O. Heflinger, C.F. Kennel, T.E. Romesser, R.L. Stenzel, A.Y. Wong and R.F. Wuerker, "Isotope separation in plasmas by use of ion cyclotron resonance," Phys. Rev. Lett. 37, 1547-1550 (1976).

Accompanying figures from:

S.L. Korn, L.N. Harnett, T.E. Romesser, and S.R. Rocklin, "PSP: The plasma separation process for isotope separation,", TRW Electronics & Defense/Quest, Winter 82/83, vol. 6.

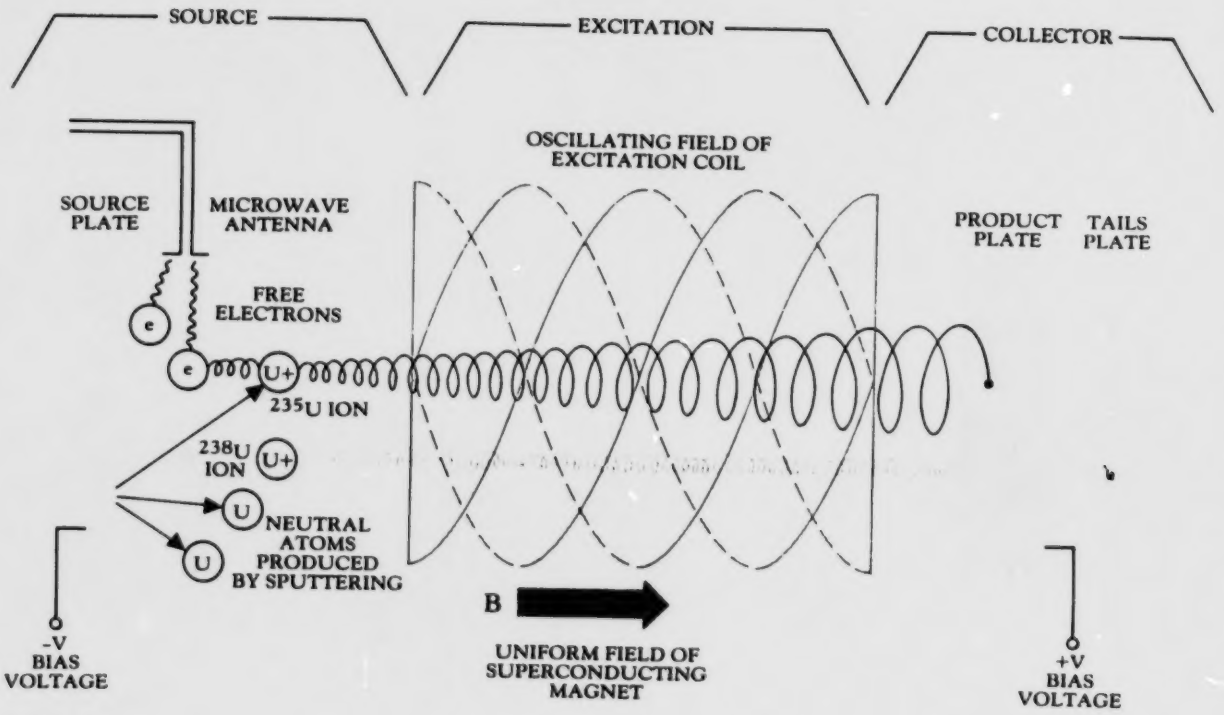


FIGURE 8

SIMPLIFIED FUNCTIONAL DIAGRAM OF THE PLASMA SEPARATION PROCESS. A uranium metal plate is the source of neutral uranium atoms to be vaporized to form the neutral plasma. The vapor is produced by bombarding the plate with energetic ions (sputtering). Ionization is produced by radiation from a microwave antenna which heats free electrons. These electrons in turn collide with neutral atoms, knocking electrons out of them and producing a plasma of positively and negatively charged particles. The plasma flows axially along the magnetic field from source to collector. The field is produced by a superconducting magnet around the outside of the cylindrical chamber. The effect of the magnet is to produce helical motion of the ions. The lighter ^{235}U ions spiral faster than the heavier ^{238}U ions — that is, they have a higher ion cyclotron frequency. As the ions move in their helical paths toward the collector, they pass through a region where an electric field, produced by an excitation coil, oscillates at the same frequency as the ion cyclotron frequency of the ^{235}U ions. This causes the radius of the helical orbit of these ions to increase, but has little effect on the heavier ^{238}U ions. The ^{235}U ions are collected by product plates placed parallel to the axis of the cylinder. The ^{238}U atoms, having much smaller helical radii, pass through the product plates and are collected by the tails plate.

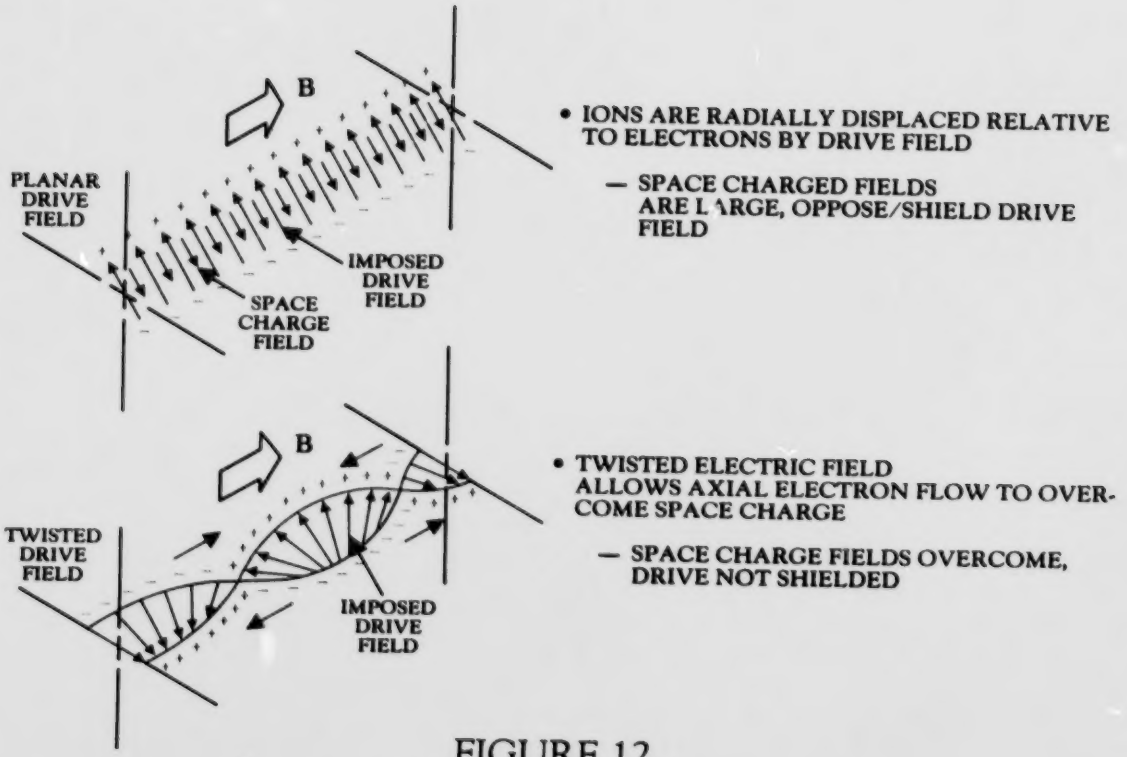

B
PLANAR DRIVE FIELD
IMPOSED DRIVE FIELD
SPACE CHARGE FIELD
• IONS ARE RADIALLY DISPLACED RELATIVE TO ELECTRONS BY DRIVE FIELD
— SPACE CHARGED FIELDS ARE LARGE, OPPOSE/SHIELD DRIVE FIELD
B
TWISTED DRIVE FIELD
IMPOSED DRIVE FIELD
• TWISTED ELECTRIC FIELD ALLOWS AXIAL ELECTRON FLOW TO OVERCOME SPACE CHARGE
— SPACE CHARGE FIELDS OVERCOME, DRIVE NOT SHIELDED

FIGURE 12

THE TWISTED SPATIAL STRUCTURE OF THE ELECTRIC FIELD produced by the helical coil allows electrons to move parallel to the magnetic field (the direction of maximum electron mobility) to overcome space charge separation effects which would otherwise reduce the drive efficiency. In the case shown at the top of the figure, the electric field is not twisted, with the result that all the driven ions are simultaneously displaced in the same radial direction. The electrons are tightly bound by the magnetic field and cannot follow the ion motion. Electric fields established by the resulting space charge effects are counter to the imposed drive field, and greatly reduce, or even eliminate, its amplitude. The lower figure shows that the ion displacement produced by the twisted electric field of the helical coil links regions of excess positive charge and excess negative charge along the same magnetic field line. Consequently electrons move axially from the negatively charged regions to positively charged regions, overcoming the space charge and the accompanying shielding effect.

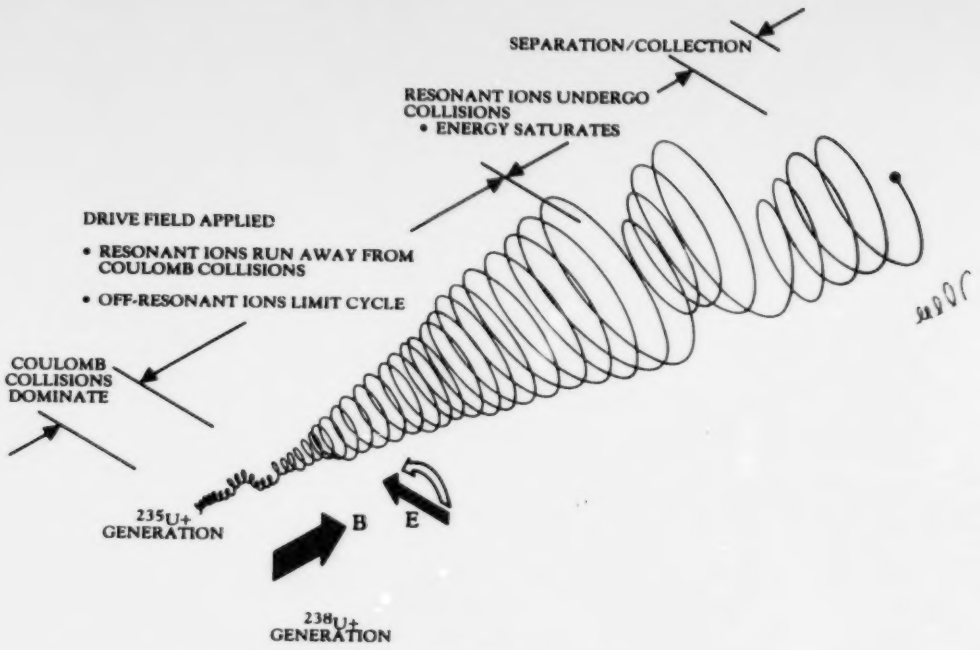


FIGURE 14

BEHAVIOR OF IONS IN THE PLASMA SEPARATION PROCESS is shown in greater detail in this sketch. When neutral atoms are ionized they are at first in a relatively low energy state, so the diameter of their helical paths is fairly small. Coulomb collisions dominate in this region. As the ions move down the cylindrical chamber they come under the influence of the oscillating field of the excitation coil. The ^{235}U ions are resonant to the frequency of this field and therefore are selectively heated, increasing the diameter of their helix and their velocity. The ions then "run away" from coulomb collisions. The off-resonant ^{238}U ions oscillate in energy, alternately increasing and decreasing their velocity and helical path diameter. This oscillation occurs at a rate determined by the difference between the frequencies of the electric field and the ion cyclotron frequency of the ^{238}U ions. At some point, the resonant ions achieve a high enough energy level that hard sphere and charge exchange collisions begin to occur and as a result, energy saturation occurs. This condition limits the plasma density and therefore the throughput that can be achieved.

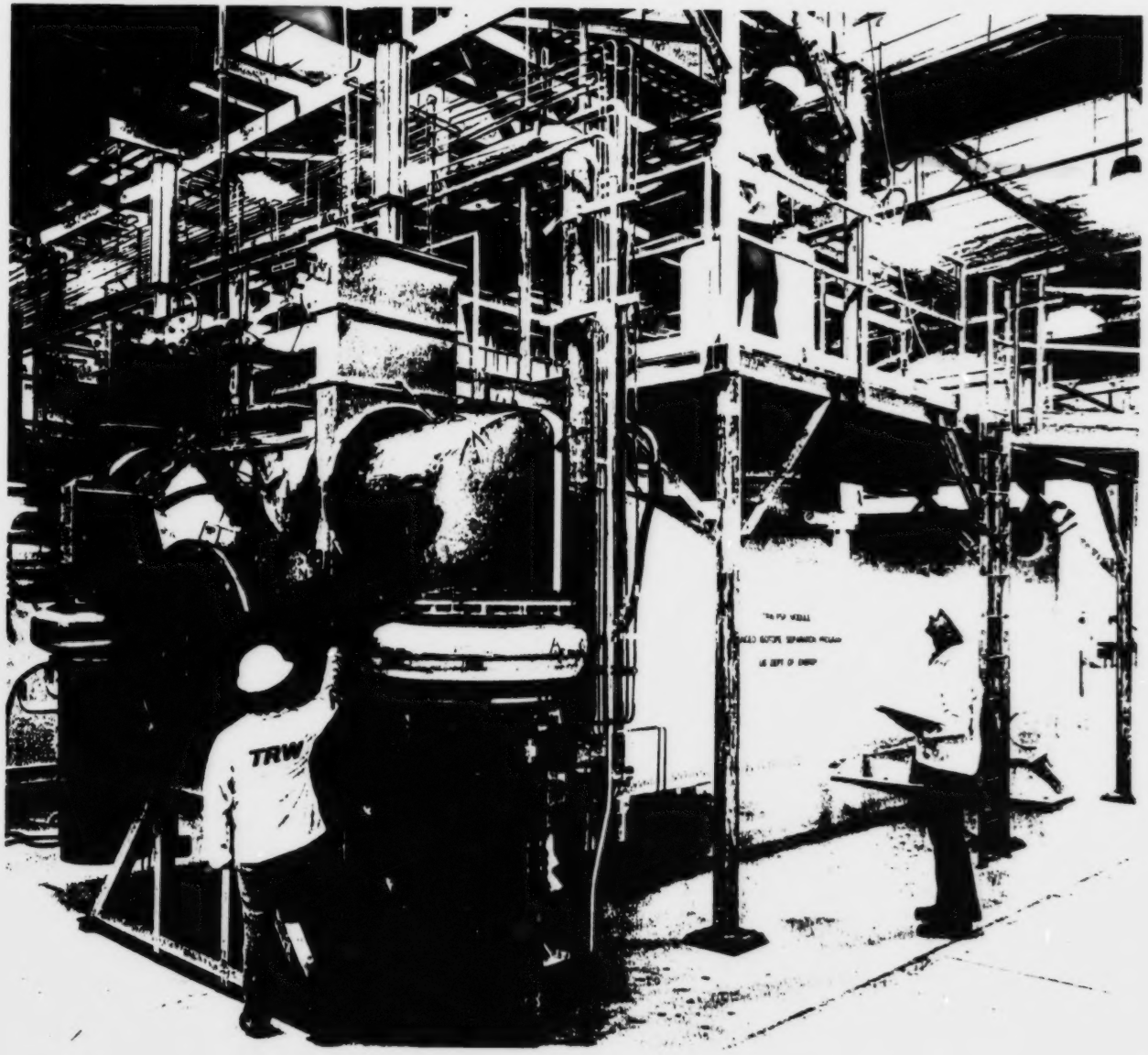


FIGURE 18

PREPROTOTYPE FACILITY FOR PSP WAS INSTALLED IN 1981, and includes a superconducting magnet built by General Dynamics with a 1-meter bore diameter and 5-meter plasma column length. The preprototype operates at ¼ scale for uranium production and full scale for most other applications. Extensive modeling and analysis have shown that the process can be scaled up to the required size without degrading performance.

A REVIEW OF POTENTIAL METHODS FOR LITHIUM ISOTOPE SEPARATION

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ABSTRACT

There is renewed interest in the separation of ^{6}Li from ^{7}Li, because of encouraging results from the world-wide effort on systems for generating power by the DT fusion reaction. Lithium at least partially enriched in ^{6}Li will be required in the tritium breeding blanket that surrounds the fusion zone in such a reactor. Published methods for lithium isotope separation are outlined and the applicability of the various available techniques to anticipated commercial production rates is discussed.

The main reasons for interest in separation of the isotopes of lithium are outlined in Figure 1. Because of the energy range of the neutrons generated by the D+T fusion reaction the cross-section for absorption of a neutron by lithium atoms to produce tritium is much greater for ^{6}Li. General categories of isotope separation methods suitable for lithium are noted in Figure 2; some details for each will be presented.

Chemical exchange systems have been widely studied since the 1930s (Figure 3). Mercury was a major component in the only production process operated in North America, in the 1950s-1960s, but alternative methods will probably be used in any future plants because of the health and environmental hazards associated with mercury. Much effort has been put into exchange systems employing new cation-complexing agents discovered since 1967 (Figure 4). The goal is to meet or exceed the magnitude of the separation factor (Figure 3) obtained for Hg-based processes. Some other chemical systems that may prove to be applicable to $^{6}Li/^{7}Li$ separation include Li/liquid NH_3, Li salt/water/polyethylene glycol solutions, and solid exchange pairs in an inert solvent (Figure 5).

Ion exchange chromatography has also been considered since the 1930s for Li isotope separation, and there is still strong interest in research in this area today (figure 6). Displacement chromatography, wherein the resin bed is saturated with the Li salt and then treated with the solution of a different cation salt to move the Li band, is preferred over elution chromatography for the indicated reasons. Scale up to industrial size plants may be possible, based on extensive Japanese data obtained over the past twenty years. Ion exchange membranes and resin-supported complexing agents also show some promise (Figure 7).

Quite recently, encouraging results have appeared for tests of laser methods for lithium (Figure 8). Both molecular Li_2 and atomic Li beams have been successfully used to demonstrate the fundamental utility of lasers to separate ^{6}Li from ^{7}Li, and agreement with theoretical calculations is good. Experiments would be required to confirm the practicality of a laser-based process. One example of the potential of rf spectroscopy was published in 1982 (Figure 9). An atomic Li beam was passed through a series of magnetic fields, one also having an rf field

tuned to either ^{6}Li or ^{7}Li as shown; an enrichment factor up to 30x was observed. The authors believed the approach could be scaled up, but so far separation has been shown only inside a mass spectrometer.

Several other approaches to lithium isotope separation have been tried. Thermal diffusion (Figure 10) is not really suitable for Li, because liquid lithium compounds don't exist, and the throughput is inherently small. Electromigration has been studied for both Li salt solutions and molten salts (Figure 10), with some degree of success. Fractional distillation and crystallization have also been shown to have some potential (Figure 11), but the economics of scale up are not known.

What is the anticipated market demand for ^{6}Li in the future? Current requirements are being met by stockpiles from the COLEX process operation. However, if DT fusion reactor technology is fully developed so as to permit construction of electricity generating stations, then estimates for ^{6}Li consumption range from about 5 to 300 Mg/a by the middle of the next century (Figure 12). With such a large demand only a few of the presently known $^{6}Li/^{7}Li$ separation techniques would be practical: chemical exchange, displacement chromatography, laser-based systems (probably), and possibly rf spectroscopy (Figure 13). The latter two are much less developed, and would require significant effort to reach the full scale demonstration stage.

THE REASON FOR INTEREST IN $^6Li/^7Li$ SEPARATION

- NATURAL ABUNDANCE 7.5% ^6Li, 92.5% ^7Li
- USES
  - ^7LiOH USED FOR pH CONTROL IN LIGHT WATER REACTORS
  - ^6LiH USED AS A SHIELD AGAINST THERMAL NEUTRONS
  - ^6Li-ENRICHED LITHIUM COMPOUNDS WILL BE REQUIRED FOR THE TRITIUM BREEDING BLANKETS FOR DT FUSION REACTORS
- NEUTRON REACTIONS

$$D + T \rightarrow {}^4He + n \quad (+17.6\ MeV)$$

$$^6Li + n \rightarrow T + {}^4He \quad (+4.8\ MeV)$$

$$^7Li + n \rightarrow T + {}^4He + n \quad (-2.5\ MeV)$$

FIGURE 2

CLASSES OF SEPARATION METHODS FOR LITHIUM

- CHEMICAL EXCHANGE SYSTEMS
  - BEFORE 1967
  - AFTER 1967 (NEW COMPLEXING AGENTS)
  - OTHER SYSTEMS
- DISPLACEMENT CHROMATOGRAPHY
  - ION EXCHANGE RESINS
  - ION EXCHANGE MEMBRANES
  - RESIN-SUPPORTED COMPLEXING AGENTS
- LASER AND RF SPECTROSCOPY
  - LASER SYSTEMS TESTED
  - SUPERSONIC ATOMIC Li BEAM
- OTHER METHODS
  - THERMAL DIFFUSION
  - ELECTROMIGRATION
  - DISTILLATION
  - CRYSTALLIZATION

FIGURE 3

CHEMICAL EXCHANGE SYSTEMS

- DISTRIBUTION OF A SPECIES BETWEEN TWO IMMISCIBLE PHASES
- AN ISOTOPE EFFECT ON THE DISTRIBUTION EQUILIBRIUM
- SEPARATION FACTOR DEFINED

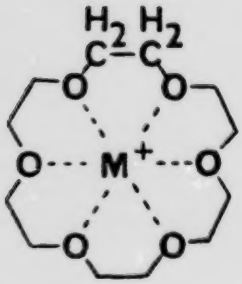
$$\alpha = \frac{([^6Li]/[^7Li])_{PHASE\ 1}}{([^6Li]/[^7Li])_{PHASE\ 2}}$$

- BEFORE 1967
  - Li SYSTEMS STUDIED SINCE THE 1930s
  - "BEST" SYSTEM USED 1950s-1960s, COLEX PROCESS, BASED ON $LiOH/H_2O$ SOLUTION CONTACTED WITH Li·Hg AMALGAM; $\alpha = 1.04^{\dagger}$ AT 50°C, $1.06^{\dagger}$ AT 0°C.
  - TODAY, HAZARDS OF MERCURY HANDLING
  - JAPANESE SCIENTISTS STILL STUDYING ORGANIC SOLVENT/Li·Hg SYSTEMS; FOR DIMETHYL SULFOXIDE, $\alpha = 1.056^{\dagger}$ AT 20°C, FOR DIMETHYLACETAMIDE, $\alpha = 1.080^{\dagger}$ AT 0°C

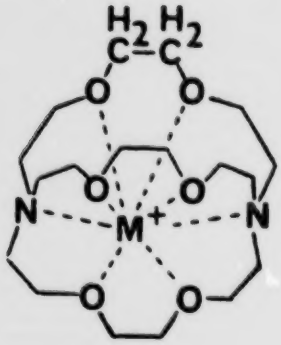
† ENRICHMENT OF ^6Li IN AMALGAM PHASE.

FIGURE 4

- After 1967
  - Discovery of "crown" type cation complexing agents (Pederson; Lehn)



18-crown-6



2,2,2-cryptate

  - Use agents with best fit for, e.g., Li^+
  - Agents soluble in organic phase increase $[Li^+]$ in that phase
  - B.E. Jepson, Monsanto-Mound Facility
    - water/chloroform
    - Li^+ trifluoracetate
    - 2,2,1 cryptand
    - $\alpha = 1.036 \pm 0.007$ at 25°C
  - Equilibrium $^6Li^+_{AQ} + {}^7LiL^+_{ORG} = {}^6LiL^+_{ORG} + {}^7Li^+_{AQ}$
  - Strong interest from Chinese scientists.

FIGURE 5

* OTHER SYSTEMS

  * GUIDE TO A LARGER α - MAXIMIZE THE <u>DIFFERENCE</u> IN ION SOLVATION CHARACTER BETWEEN THE TWO PHASES; BEST SYSTEM WILL HAVE A CHANGE IN OXIDATION STATE.

  * ALKALI METAL/LIQUID AMINE SYSTEMS OFTEN EXHIBIT A PHASE SEPARATION AT LOW TEMPERATURE; E.G., LI IN NH_3 (LIQ) AT -33°C NORMAL SOLUTION, BUT BETWEEN -63 AND -78°C AND 2-8 MOLE % LI A SECOND METALLIC-LIQUID PHASE FLOATS ON THE SOLUTION; α=1.01 AT -76°C, ^{6}LI IN NEW PHASE.

  * WATER/PEG 3000 SYSTEMS FORM TWO PHASES AT HIGH SALT CONCENTRATIONS, E.G, 18 WT% $(NH_4)_2 SO_4$; NO WORK ON LITHIUM; ADVANTAGE - "TOXIC, VOLATILE, COMBUSTIBLE, OR DANGEROUSLY EXPLOSIVE" ORGANIC SOLVENTS CAN BE AVOIDED.

  * REACTION $^7LI_S + {}^6LIF_S = {}^6LI_S + {}^7LIF_S$

    FOUND K = 1.10 IN ELECTROCHEMICAL REVERSIBLE DOUBLE CELLS CONTAINING KBF_4 IN PROPYLENE CARBONATE; PROBLEM OF LIMITED CHEMICAL STABILITY.

DISPLACEMENT CHROMATOGRAPHY

- Ion Exchange Resins
  - DISTRIBUTION OF IONS BETWEEN A MOVING LIQUID PHASE AND A STATIONARY SOLID PHASE
  - CAN GET AN ISOTOPE EFFECT - Li SYSTEMS STUDIED SINCE 1930s, STILL INTEREST TODAY
  - DISPLACEMENT PREFERRED OVER ELUTION CHROMATOGRAPHY FOR HIGHER THROUGHPUT; SACRIFICE SPECIFIC SEPARATION EFFECT
  - SELF-SHARPENING EFFECTS OCCUR AT BAND BOUNDARIES, WITH ENRICHMENT OF LIGHTER ISOTOPE AT REAR EDGE
  - α ONLY A FEW TENTHS OF A PERCENT FOR $^6Li/^7Li$, BUT HETP SMALL SO SERIES OF COLUMNS EFFECTIVE

EXAMPLE: H^+ RESIN

1. COLUMN FIRST SATURATED WITH Li SALT, WASHED TO REMOVE ANIONS
2. Li^+ IONS DISPLACED BY, E.G., Ca^{++} (ACETATE)
3. AFTER 75 BAND LENGTHS 97.1% ^7Li AT FRONT BOUNDARY, 14.6% ^6Li AT REAR

- JAPANESE SCIENTISTS BELIEVE LARGE SCALE SYSTEM CAN BE SET UP, PLANS FOR 100 KG ^7Li/A PLANT.

FIGURE 7

- Ion Exchange Membranes
  - Cation exchange membrane pulled slowly through electromigration cell, from aqueous anode region through inert organic fluid (CCL_4)
  - Li^+ ion is the current conductor, ^6Li enriched at front of band moving toward anode, negligible remixing of ions
  - Ratio of ion mobilities $^6Li/^7Li = 1.0037$
  - With displacement by Ca^{++} salt, 3 cm band moved 74 cm, 13.4% ^6Li at band front
  - Enrichment falls rapidly away from front

- Resin-supported Complexing Agents
  - Crown or cryptand species attached to polymer structure (beads)
  - Resin saturated with Cs^+, then Li^+ band loaded, displaced with Na^+ acetate/methanol
  - Larger α, 1.014 at 40°C, but column efficiency no better than for ion exchange; $^6Li^+$ enriched at rear boundary; used the [2-benzo.1.1] cryptand
  - Chromatography? Single stage contact using $LiCl$ and [2-benzo.2.2] cryptand gave α 1.046 at 0°C with methanol solution; ^6Li enriched in resin phase (1984)

LASER AND RF SPECTROSCOPY

- LASER SYSTEMS
  - EXPERIMENTAL AND THEORETICAL RESULTS HAVE APPEARED ONLY SINCE 1978
  - ONLY SMALL SCALE, "IN-MASS-SPECTROMETER" TESTS
  - MATHUR ET AL.
    - TWO-PHOTON EXCITATION/IONIZATION OF Li_2 SPECIES IN MOLECULAR LITHIUM BEAM, WITH CW ARGON ION LASERS (Li ATOMS NOT INVOLVED)
    - MEASURED $^6Li_2^+$, $^6Li^7Li^+$ AND $^7Li_2^+$ BY MASS SPEC.
    - AT 465.8 NM $\longrightarrow$ 100% $^6Li_2^+$
    - AT 476.5 NM $\longrightarrow$ EITHER $^6Li^7Li^+$ OR $^7Li_2^+$
  - THEORETICAL CALCULATIONS IN AGREEMENT, PREDICT WIDE RANGE OF SPECTRAL WAVELENGTHS SUITABLE
  - JAPANESE WORK ON TWO-STEP PHOTOIONIZATION OF AN ATOMIC LITHIUM BEAM, WITH DYE LASER AS EXCITER AT 670.8 NM AND ND:YAG LASER AS IONIZER AT 260.0 NM
  - > 90% ^6Li ENRICHMENT USING 2-10 W/cm^2, GOOD AGREEMENT WITH CALCULATIONS
  - JAPANESE PATENT 1983 DECEMBER TO JAERI, LASER-BASED PROCESS FOR ISOTOPE SEPARATION INCLUDING LITHIUM

FIGURE 9

- RF SPECTROSCOPY (1982)
  - COLLIMATED SUPERSONIC ATOMIC LITHIUM BEAM PASSED THROUGH AN INHOMOGENEOUS GRADIENT MAGNETIC FIELD TO ALIGN SPINS OF PARAMAGNETIC SPECIES
  - BEAM THEN DIRECTED THROUGH 1.5 G HOMOGENEOUS FIELD CONTAINING RF ANTENNA TUNED TO ^{6}Li (228.528 MHz) OR ^{7}Li (3.191 MHz) SPECIES TO CAUSE SPIN FLIPPING
  - FINALLY, BEAM PASSED THROUGH ANOTHER GRADIENT FIELD TO FOCUS THE SPIN-REVERSED SPECIES ONTO THE DETECTOR
  - ENRICHMENT FACTORS UP TO 30 OBSERVED
  - SCALE-UP POSSIBLE VIA MULTIPLANAR SUPERSONIC BEAMS?

OTHER METHODS

- THERMAL DIFFUSION
  - TENDENCY OF ISOTOPIC SPECIES TO SEPARATE ALONG A THERMAL GRADIENT; LIGHTER ISOTOPE USUALLY MIGRATES TO HOTTER ZONE
  - PURE LIQUID CHEMICAL PREFERRED, E.G., CS_2 FOR S OR CH_3Cl FOR Cl, WHICH IS HELD IN THE NARROW ANNULUS BETWEEN TWO CONCENTRIC TUBES MAINTAINED AT DIFFERENT TEMPERATURES
  - AQUEOUS SOLUTION AN ACCEPTABLE ALTERNATIVE
  - ONLY RESULTS FOR Li BASED ON MOLTEN SALTS, WITH ^6Li TO HOTTER ZONE BETWEEN TWO METAL PLATES AT 268 AND 425°C; $\alpha = 1.0049$
  - LIMITATION - PRODUCTION RATE A FEW KG/A
- ELECTROMIGRATION
  - ELECTROLYSIS OF LiCl IN WATER OR ETHANOL, AT MERCURY ELECTRODE, GIVES ELECTROLYTIC SEPARATION COEFFICIENT OF 1.055 ± 0.005 (TEMPERATURE INDEPENDENT)
  - ADVANTAGES OF MOLTEN HALIDES - HIGHER CATION MIGRATION VELOCITY, HIGHER CURRENT, WIDER TEMPERATURE RANGE → HIGHER OVERALL ENRICHMENT FACTOR
  - E.G., LiCl IN CELL AT 625-1375°C - ^7LiCl CONCENTRATES AT THE ANODE, ^6Li METAL REACTS WITH RECYCLED Cl_2 AT THE HOLLOW GRAPHITE CATHODE

- DISTILLATION
  - GOOD METHOD IN GENERAL, BUT NO "LIQUID" LITHIUM COMPOUNDS EXIST; MOST STABLE SALTS MELT ABOVE 400°C
  - SOME STUDIES DONE WITH LIQUID LITHIUM METAL, M.P. - 180°C, IN 1950S USING SHORT PATH VACUUM DISTILLATION COLUMNS
  - SINGLE STAGE SEPARATION FACTORS 1.052-1.064 FOR 535-627°C POT TEMPERATURE IN MULTI-STAGE STAINLESS STEEL STILLS
  - ECONOMICS?

- CRYSTALLIZATION
  - ISOTOPE-SELECTIVE, CONTROLLED PRECIPITATION OF LITHIUM SALTS OR COMPLEXES FROM WATER SOLUTION (TWO PATENTS)
  - E.G., $(NH_4)_2\,CO_3$ ADDED AS PRECIPITATION AGENT TO SOLUTION OF LITHIUM ALUMINUM OXALATE COMPLEX; FIRST FRACTION ENRICHED IN ^7Li TO 30X
  - MULTIPLE FRACTIONATION STEPS CLAIMED POSSIBLE, BUT FEW DETAILS GIVEN IN ABSTRACTS
  - SOME EXAMPLES OF Li_2Co_3 PRECIPITATION GIVEN IN A PATENT (1961)

PROCESSES SUITABLE FOR "LARGE" SCALE $^6Li/^7Li$ SEPARATION

- POSSIBLE DEMAND FOR ^6Li?
  - BASED ON STARFIRE, 1200 MW_E, T_2 PRODUCTION RATE - 1 KG/DAY, SO CONSUME - 2 KG/DAY ^6Li
  - FOR SYSTEM OF 10 SUCH REACTORS ANNUAL BURNUP OF ^6Li WOULD BE - 7 MG
  - 1978 REPORT PREDICTED 46 TO 276 MG ^6Li/A FOR 11,500 MW_E INSTALLED IN 2020

- CANDIDATES?
  - SMALL SCALE ONLY
    - THERMAL DIFFUSION
    - ELECTROMIGRATION (MOLTEN SALTS)
    - ELECTROMAGNETIC MASS SEPARATOR (CALUTRON)
  - LARGE SCALE POSSIBLE
    - TWO PHASE CHEMICAL EXCHANGE
    - DISPLACEMENT CHROMATOGRAPHY
    - LASER-BASED PROCESS?
  - UNKNOWN POTENTIAL
    - RF SPECTROSCOPY

FIGURE 13

CONCLUSIONS

- IF FUSION REACTORS BECOME A REALITY IN THE NEXT CENTURY FOR POWER GENERATION, DEMAND FOR ^{6}Li WILL LIKELY EXCEED 5 MG/A.
- PROCESSES BASED ON CHEMICAL EXCHANGE AND/OR DISPLACEMENT CHROMATOGRAPHY WILL PROBABLY PROVIDE THE FIRST ENRICHED ^{6}Li
- LASER- AND/OR RF SPECTROSCOPY-BASED PROCESSES COULD PROBABLY BE DEVELOPED TO PROVIDE "LOW" COST ^{6}Li ENRICHMENT.

ACKNOWLEDGEMENTS

CFFTP — FOR PARTIAL FUNDING OF OUR LITHIUM WORK UNDER THE FUSION BREEDER BLANKET PROGRAM

LLYNNE PLANTE — THE LABORATORY WORK ON LITHIUM CHEMISTRY

JIM HALLIDAY, KEN FRANKLIN — THE LOCAL NMR EXPERTS, FOR ADVICE

COPIES OF THE FULL REVIEW ARE AVAILABLE

- JOINT CFFTP/AECL REPORT
  No. CFFTP-G-85036/AECL-8708
- REVIEW ARTICLE ACCEPTED BY SEPARATION SCIENCE AND TECHNOLOGY 1985 APRIL.

CARBON-14 ENRICHMENT - STATUS REPORT

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INTRODUCTION

Carbon-14 is produced as a by-product of the operation of CANDU reactors. It is in a dilute form contaminated with ^{12}C. This ^{14}C can be regarded as nuclear waste which represents a challenging disposal problem for Ontario Hydro because of its very long half-life, or it can be regarded as an extremely valuable by-product of the operation of CANDU reactors which offers a marketing opportunity for Ontario Hydro. I will say a few words about the supply and demand situation for ^{14}C and spend most of the talk describing the status report on our laser and cryogenic distillation ^{14}C enrichment research programs. As we have previously reported our ^{14}C laser isotope results, more time will be given to describing our cryogenic distillation experiments. A brief description of a possible full scale ^{14}C enrichment facility will be given.

Table 1 lists those who have contributed to the Research Division ^{14}C enrichment programs. Those working on isotope separation technology are in the Electrical Research Department. Those working on the recovery of ^{14}C from CANDU reactors are in the Chemical Research Department.

In Figure 1 the schematics of the ^{14}C market are shown. The ^{14}C market has only two primary suppliers, AECL and Russia, which produced about 120 g/a in 1983. With a wholesale price of about $15 000/g, this market had a value of about $1 800 000/a in 1983 and is reported by one of the ^{14}C retailers to be growing by about 10%/a. The reason ^{14}C is so expensive is that currently it is made by irradiating an aluminum nitride target in a reactor for 4.5 years. Carbon-14 is sold to a handful of retailers as $Ba^{14}CO_3$ at the 85-95% ^{14}C level. These retailers synthesize ^{14}C labelled compounds which sell for $2 300 000/g or more and are used as tracers for carbon in medical and biological research. Even repackaged $Ba^{14}CO_3$ retails for more than $250 000/g of ^{14}C.

Ontario Hydro produces about 10 times the current demand for ^{14}C and by the time Darlington is completed will be producing about 25 times the current world demand. It is an unavoidable by-product of CANDU nuclear power stations. Most of the carbon is produced by an n-alpha reaction on ^{17}O in the moderator water. Almost all of this is retained in the ion exchange resin, but a little escapes to the moderator cover gas where it can escape to the atmosphere. This ^{14}C, along with other carbon isotopes, can be retained by a calcium hydroxide absorber developed by the Research Division. The first recovery unit will be installed on a CANDU reactor later this year. For reactors which use nitrogen annulus gas (Pickering A), ^{14}C is also produced in the annulus gas. The portion of this ^{14}C which is in the gas phase could be retained by a system similar to the cover gas recovery system. Most of the ^{14}C ever produced by Ontario Hydro is stored in the spent ion exchange resin. This stored ^{14}C inventory can be regarded either as a serious long-term disposal problem for Ontario Hydro (stocks will decay away to negligible levels in about 200 000 years) or can be regarded as a marketing opportunity for Ontario Hydro analogous to the planned marketing of tritium. A method of recovering ^{14}C from ion exchange resin is being demonstrated by the Research Division. The ^{14}C is recovered from CANDU reactors as carbon dioxide containing approximately 2% ^{14}C.

LASER ISOTOPE SEPARATION OF ^{14}C

We have investigated two methods of enriching ^{14}C to the 90% level required for marketing: laser isotope separation and cryogenic distillation. In laser isotope separation the $^{14}CO_2$ is converted to a molecule such as formaldehyde which has a much stronger optical absorption at 352.2 nm in the ^{14}C bearing molecule than in the ^{12}C bearing molecule (Figure 2). The $^{14}CH_2O$ is selectively dissociated by laser light into hydrogen and carbon-monoxide, which can be readily separated from the undissociated $^{12}CH_2O$. With a laser linewidth equal to the width of the absorption line, single step enrichments of 250 times have been observed. When the laser line is narrowed by a factor of 5, the enrichment increases to 1180, the largest single step enrichment ever observed for ^{14}C using any molecule and any laser. An enrichment factor of about 450 is required to enrich ^{14}C from 2% to 90% in a single step.

Figure 3 shows how isotopic enrichment declines as one tries to remove more and more carbon-14 from a gas sample. This data is for the unnarrowed laser line. Using the narrowed line the curve is shifted upward by about a factor of 4. The curve would not be expected to fall off as rapidly with depletion if the gas in the absorption cell were illuminated uniformly. Using a narrowed laser line, we can not expect better than 40% ^{14}C depletion of a formaldehyde gas sample and still enrich from 2% to 90% in a single step.

CRYOGENIC DISTILLATION OF ^{14}C

In figure 4 we see a schematic of the cryogenic still built at the Research Division. The active element is the narrow (3/4" diameter) tube coming down from the lower liquid nitrogen reservoir. The throughput capability of this still is enough to meet current world demand for ^{14}C. However, the column length would need to increase by about an order of magnitude to meet the enrichment requirements of the market place.

The reboiler at the bottom of the column is powered by two 36 watt heaters. The temperature of the reboiler is measured using silicon diode temperature sensors capable of 0.05K resolution at 70K. The column and condensers are insulated with 60 layers of aluminized Mylar film. The effective temperature isolation is equivalent to 60 concentric thermos bottles. The high vacuum (approximately 10^{-10} atmospheres), required for thermal insulation of the column and condenser, is maintained by an ion pump connected to the piping surrounding the column. The liquid nitrogen which cools the cryogenic column comes from a large external reservoir (not shown) where it is stored at 28 psi (87 K). During still operation the nitrogen surrounding the condenser in the lower reservoir is maintained at temperatures as low as 67 K with a reproducibility of 0.1 K by reducing the pressure in the reservoir with vacuum pumps and a microprocessor controlled valve. In order to top up this reservoir with liquid nitrogen from an 87 K supply without upsetting the condenser temperature, a 5 L intermediate reservoir was installed above the distillation unit. When a sensor in the lower reservoir calls for refilling, the upper reservoir is automatically filled and the pressure and temperature of the liquid nitrogen in this reservoir are adjusted until they match conditions in the lower reservoir. This liquid nitrogen is then automatically transferred to the lower reservoir with a condenser temperature upset of no more than 0.1 K.

Isotope separation by cryogenic distillation is based on the fact that there is a difference in vapour pressure between isotopically substituted molecules. This effect is largest when the molecule is small and the isotopically substituted atom is light. The best molecule for carbon

isotope separation is carbon monoxide (CO). When liquid CO is in equilibrium with gaseous CO, the ^{12}C content of the vapour is always greater than the ^{12}C content of the liquid due to this vapour pressure difference. Figure 5 illustrates why it may be useful to operate the cryogenic distillation column with the liquid nitrogen coolant below the 87 K temperature of the large external liquid nitrogen reservoir and below the 77 K of liquid nitrogen at atmospheric pressure. The vapour pressure ratio (alpha) of $^{12}C^{16}O$ to the other eight isotopically substituted CO molecules increases dramatically with decreasing temperature. In the cryogenic distillation column the CO is vaporized at the bottom of the column. The vapour moves up the column and is condensed at the top of the column and returned back down the column as a liquid. Each time the ascending vapour equilibrates with the descending liquid the ^{14}C content of the liquid increases by alpha, the vapour pressure ratio. This equilibration occurs every 2 or 3 cm along the column. In principle, we can achieve any ^{14}C enrichment we desire by just lengthening the column. Large alphas are desirable to reduce the overall length of the column and to reduce the inventory of radioactive ^{14}C in the enrichment facility. Figure 6 illustrates a calculation of how the ^{12}C, ^{13}C and ^{14}C concentrations expressed as mole fractions are expected to vary along the length of a cryogenic distillation column. Note that the ^{13}C impurity in the CO peaks in concentration in the middle of the column, while the ^{12}C and ^{14}C concentrations increase or decrease along the entire length of the distillation column.

As the reboiler power in watts increases, the pressure drop (and temperature gradient) across the column increases. At about 52 watts the pressure drop begins to rise very rapidly because the vapour in the column is moving so rapidly that the liquid returning to the column from the condenser is unable to flow downward against the vapour flow. Under this condition we say that the column has "flooded". Most distillation columns are operated at about 70% of the wattage required for flooding. The curve in Figure 7 indicated by solid circles shows how the CO inventory in the column and condenser varies with the amount of power going to the reboiler. The condenser is a vertical copper tube with an inventory of about 1 cc so that the curve really reflects changes in the CO inventory in the column. Inventories rise slowly as the vapour velocity increases and start to climb very rapidly just before the flooding condition is reached. Note that after flooding the column inventory at all power levels is 16-18% higher (open circles) than before flooding (closed circles). We interpret this to mean that the packing is more uniformly wetted (some dry spots are eliminated) after flooding.

CARBON-14 ENRICHMENT PROCESSES

Figure 8 briefly summarizes possible cryogenic distillation and laser isotope separation ^{14}C flow sheets. Recall that ^{14}C can be recovered from CANDU reactors or from their ion exchange resin wastes as carbon dioxide. In general, it will be immobilized as solid calcium carbonate ($CaCO_3$) which can be transported to the ^{14}C enrichment facility. Heat can produce a stream of carbon dioxide gas which can be quantitatively converted to CO by passage over hot (400 C) zinc powder prior to being fed into the cryogenic distillation column. The product enriched to 90% ^{14}C is oxidized to carbon dioxide and precipitated as barium carbonate ($BaCO_3$), an extremely low vapour pressure solid and the safest form for storing and shipping ^{14}C. The final oxidation and precipitation steps are identical to those currently used for all ^{14}C production. Note that the distillation step can be modified to accommodate almost any conceivable carbon-14 feed concentration, product concentration, and waste concentration by modifying the length of the column and the position of the feed point. A column built with excess length and multiple feed points could accommodate a wide variety of feed, product, and waste specifications.

The laser process starts with a carbon dioxide stream generated from calcium carbonate as described above. Formaldehyde (CH_2O) synthesis from CO_2 requires two steps. We have demonstrated synthesis of small quantities of formaldehyde using CO as the intermediate compound. This method is ideal for enriching small (50 mg) samples. We intend to use this method and small enrichment levels (10 times) to extend the range of radiocarbon dating to samples that are about 20 000 years older than what can be measured today. NASA has developed a reaction sequence using methane as the intermediate to convert carbon dioxide from breathing air to formaldehyde as a first step in converting wastes into food. We have not done any work in this area, but we believe that the approach chosen by NASA may be the best way to convert large quantities of carbon dioxide to formaldehyde. The formaldehyde is admitted to a large absorption cell in which a laser selectively dissociates the ^{14}C containing molecules giving a stream of H_2 and CO enriched in ^{14}C which can be readily separated from the formaldehyde. If the feed is at least 2% ^{14}C and if no more than 40% of the ^{14}C in the feed need be recovered, one enrichment step is sufficient. Otherwise, the CO and H_2 can be converted directly to formaldehyde in a single step synthesis that we have demonstrated in the laboratory and the enrichment and separation steps can be repeated. The final CO product can be oxidized and precipitated as barium carbonate as described above.

Table 2 gives an approximate description of a ^{14}C cryogenic distillation plant. We are currently engaged in a program to select the best column packing and operating procedures. Our research column is 147 cm long and we have measured up to 110 plates of separation with this column at low boil-up rates. This represents a height of an equivalent theoretical plate (HETP) of about 1.4 cm. The plate height increases as the boil-up rate increases to the flooding rate. We believe that plate heights of 2 to 3 cm can be achieved at the most efficient operating conditions. This means that the column would have to be from 13 to 19 m long to enrich ^{14}C from 2% to 90%. The ^{14}C inventory of the cryogenic distillation column would be about 200 Ci. Reducing the diameter of the bottom half of the column to 9 mm would reduce the ^{14}C inventory of the column to as low as 60 Ci. Two or three packings will be tested under a wide variety of operating conditions before the plant design is recommended. Table 3 gives crude estimates for the cost of a ^{14}C cryogenic distillation plant. For isotopes with modest demand like ^{14}C it is important that the plant be automated as much as possible to reduce labour costs and much of our research program is devoted to developing automation systems. The cost of producing ^{14}C from reactor wastes should be substantially below the cost of producing ^{14}C by irradiating targets in a reactor for 4.5 years.

CONCLUSIONS

The laser method of enriching ^{14}C has the highest (1180) single step enrichment factor, extremely low ^{14}C inventories in the enrichment step, and is the only system applicable to enrichment of micro samples to enhance radiocarbon dating. The chemical synthesis steps and staging are more difficult than for cryogenic distillation.

Cryogenic distillation is a proven technology in that all ^{13}C is made this way although enrichment of ^{14}C by this method to date has only been done in our computer. Our research program is designed to demonstrate that cryogenic distillation is also an appropriate enrichment method for ^{14}C. It has a fairly low ^{14}C inventory, requires minimal chemical synthesis, and permits the specification of additional enriching, stripping, or changes in the feed ^{14}C concentration by simply specifying additional column length and provision for multiple feed points. The distillation process is easily automated and can make use of operation and maintenance skills already available in operating divisions of Ontario Hydro.

Carbon-14 can be regarded as a serious waste disposal problem or as a marketing opportunity for Ontario Hydro. Enrichment either by laser or by cryogenic distillation is technically feasible. An enrichment plant that is only pilot plant size could produce the entire world requirement for ^{14}C. All of the required technology is well on the way to being demonstrated at Ontario Hydro's Research Division.

TABLE 1

CARBON 14 ENRICHMENT PROGRAM - RESEARCH TEAM

CRYOGENIC DISTILLATION	
STILL DESIGN AND CONSTRUCTION	KEN WOODALL, DAVE BELLAMY
CALCULATIONS - ISOTOPIC PROPERTIES	FRANK BARTOSZEK
CHEMICAL CONVERSIONS	KEN WOODALL, JEFF ROBINS
AUTOMATION	FRANK BARTOSZEK, BERRY FRADLEY
ANALYTICAL SYSTEMS	JEFF ROBINS
STILL MODELLING	AZIZ AHMED - U OF T
LASER ISOTOPE SEPARATION	
ENRICHMENT STUDIES	LEN MANNIK, STU BROWN
CHEMICAL CONVERSIONS	KEN WOODALL, STU BROWN, RHEINHART GNOYKE
CARBON 14 RECOVERY	
RESIN STRIPPING	BABU NOTT
COVER GAS/ ANNULUS GAS RECOVERY	CHRIS CHEH

1. MARKET DETAILS

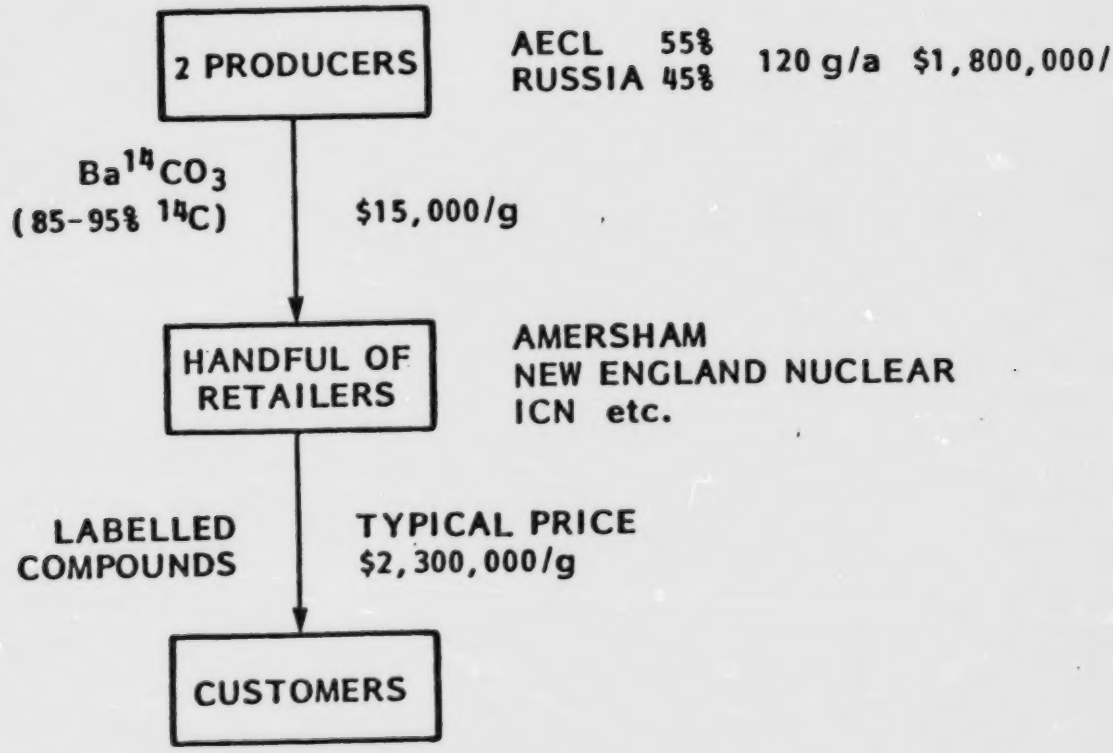


FIGURE 1

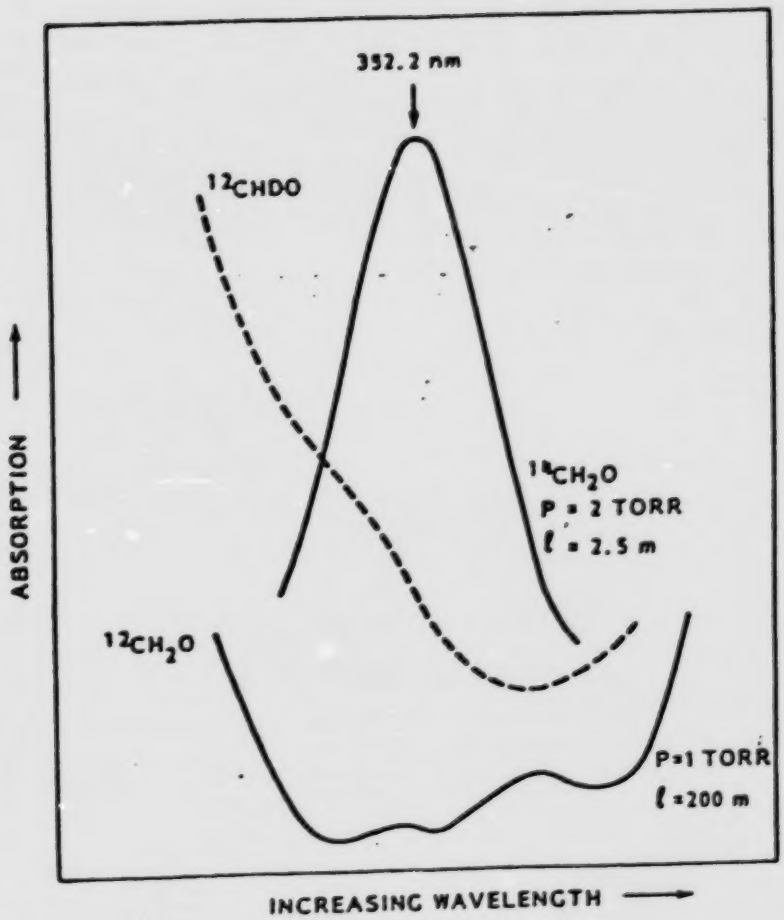
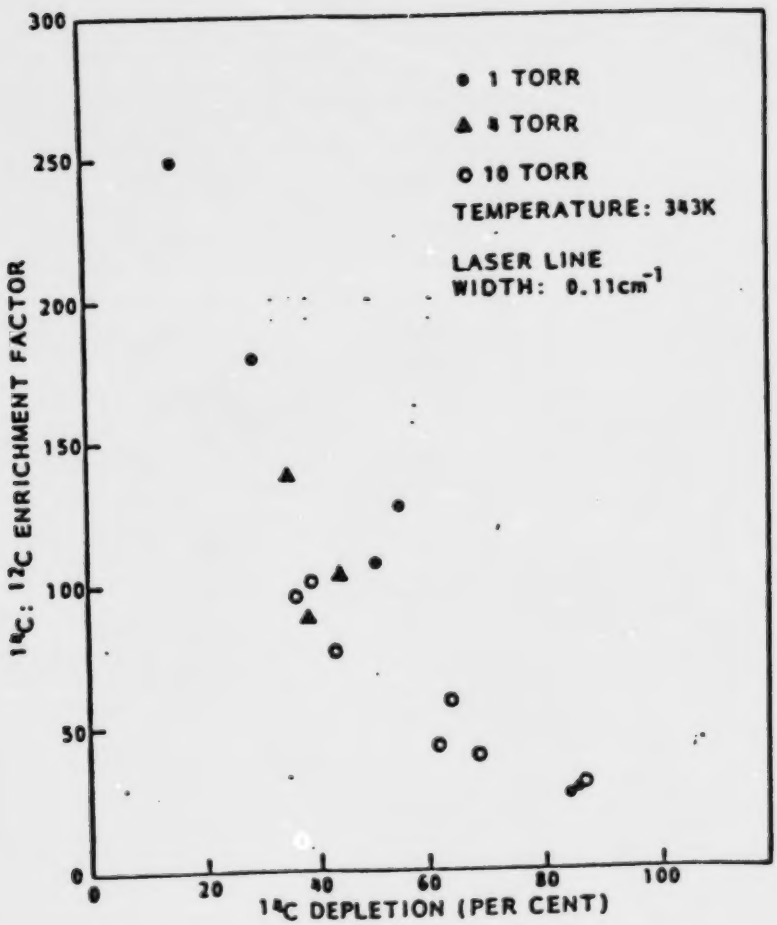

352.2 nm
$^{12}CHDO$
$^{13}CH_2O$
P = 2 TORR
ℓ = 2.5 m
$^{12}CH_2O$
P=1 TORR
ℓ =200 m
ABSORPTION
INCREASING WAVELENGTH

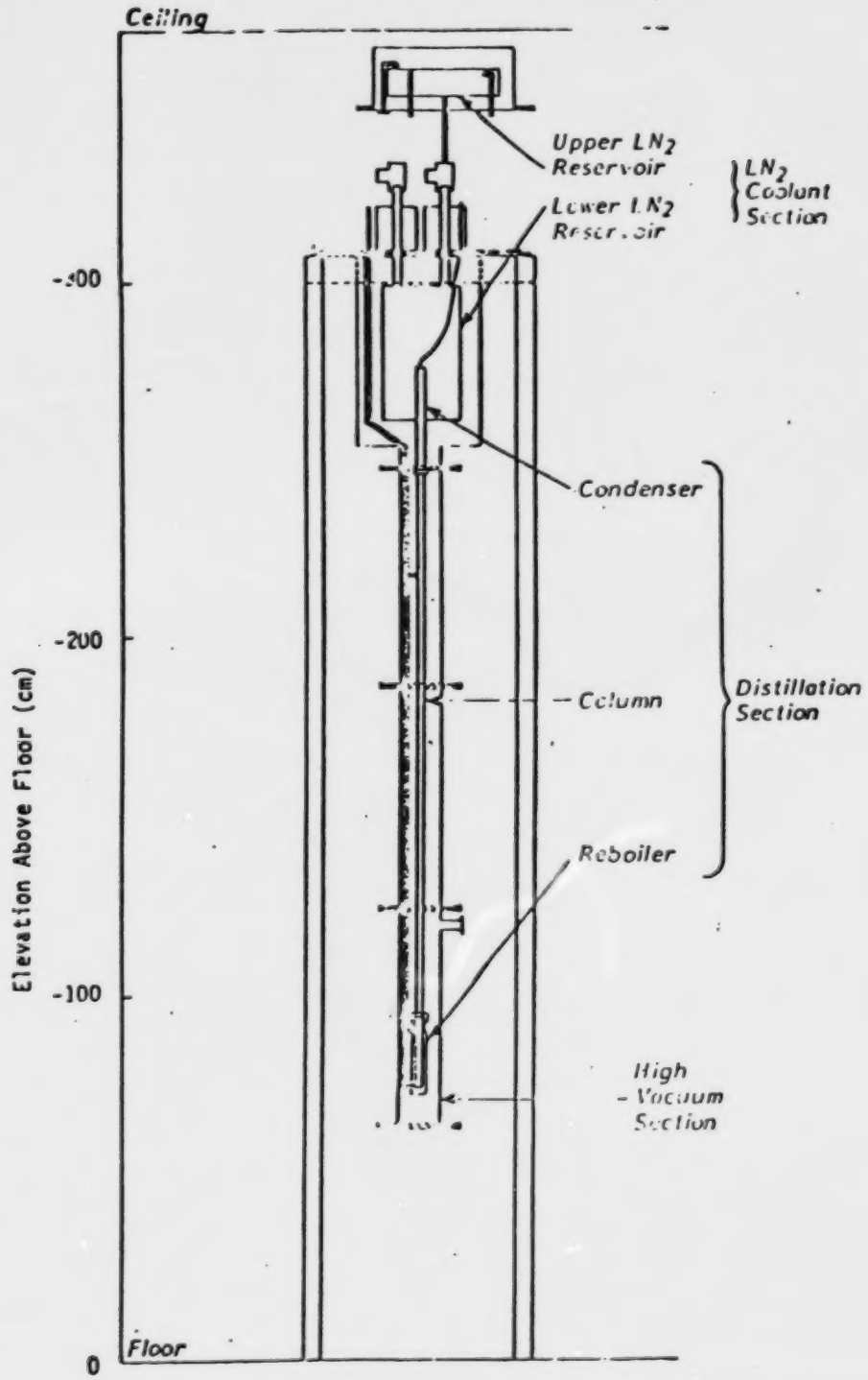
FIGURE 2



DEPENDENCE OF THE ^{14}C:^{12}C ENRICHMENT FACTOR ON CARBON-14 DEPLETION

FIGURE 3

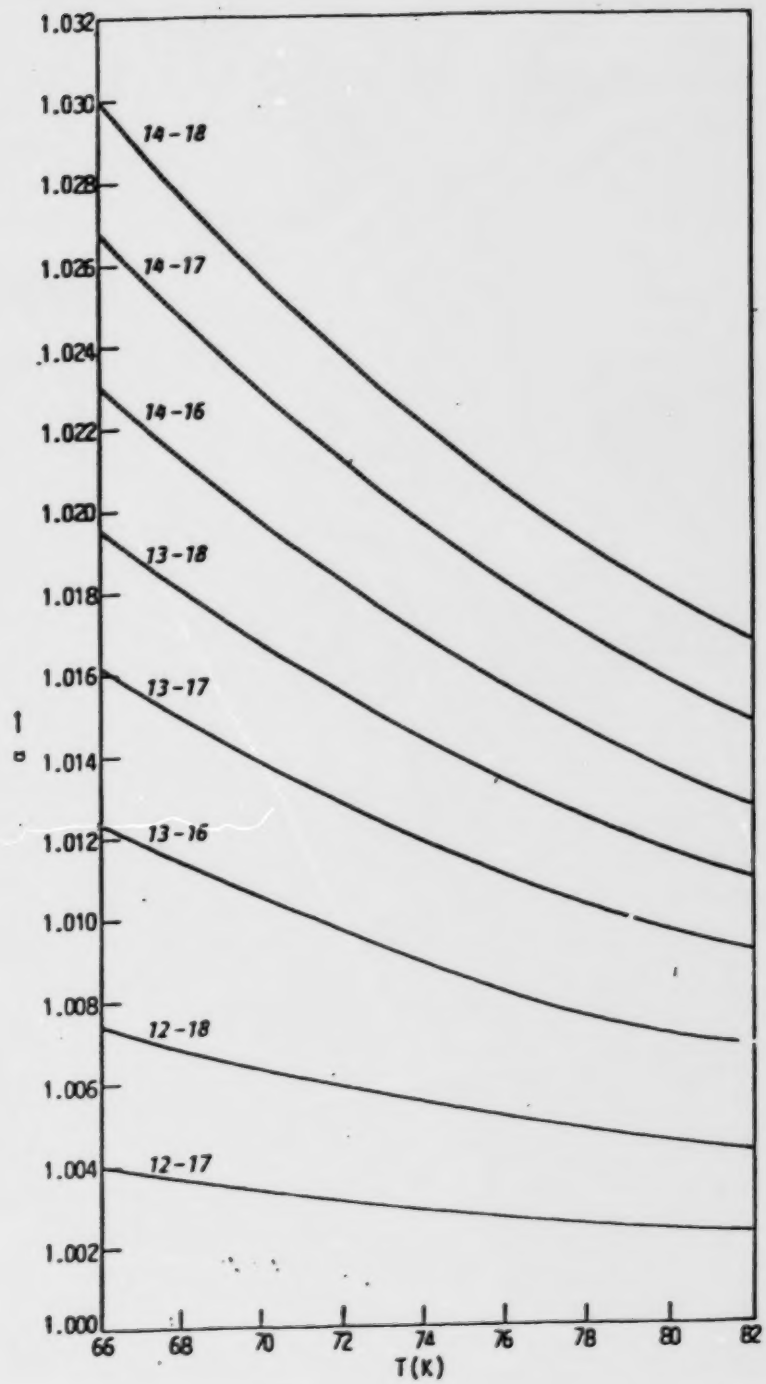
88-99



CRYOGENIC DISTILLATION DEMONSTRATION UNIT

FIGURE 4

88-99



TEMPERATURE DEPENDENCE OF THE SEPARATION FACTORS FOR ISOTOPIC CARBON MONOXIDE. THE SYMBOLS 12-17 REFER TO $^{12}C\ ^{17}O$, etc.

FIGURE 5

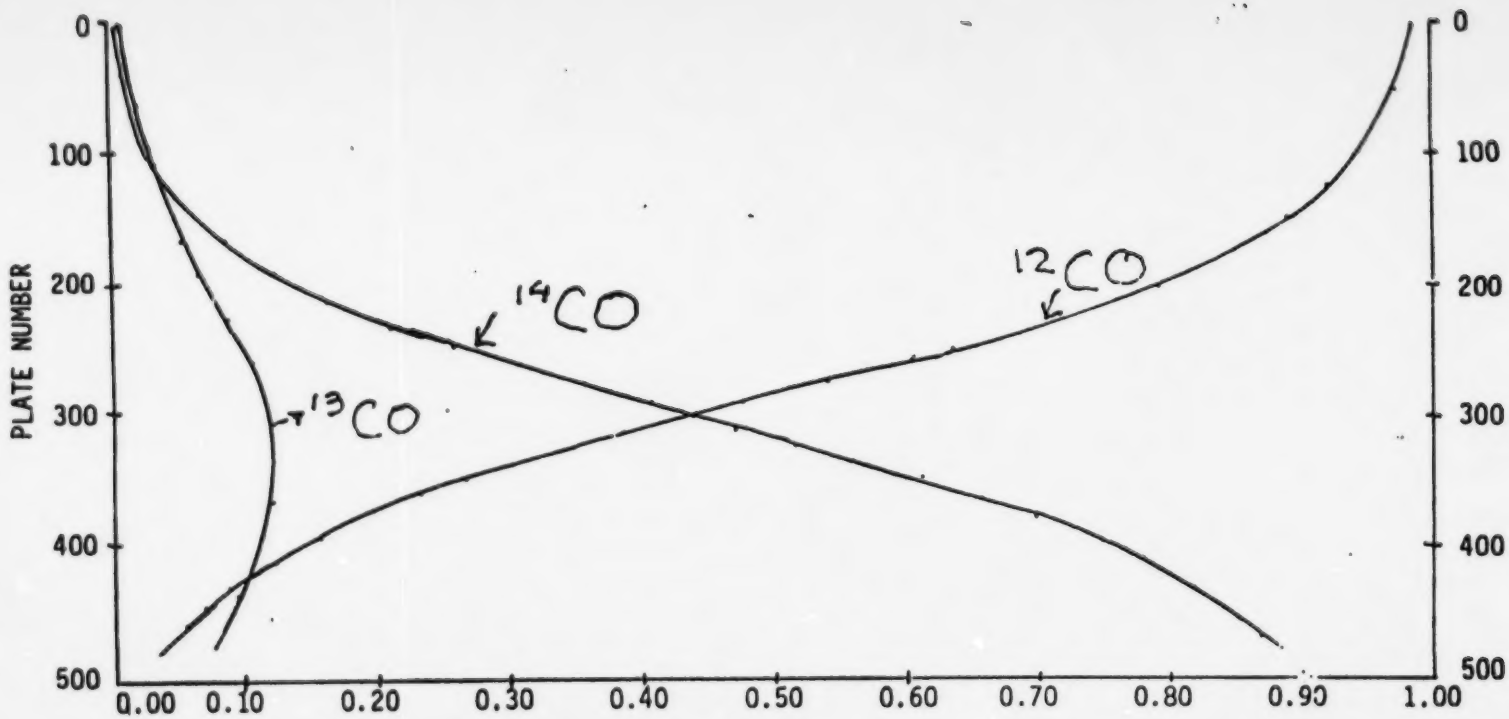


FIGURE 5

Figure : Concentration Profile for ^{13}CO Distillation as Predicted by the Lewis-Matheson Method

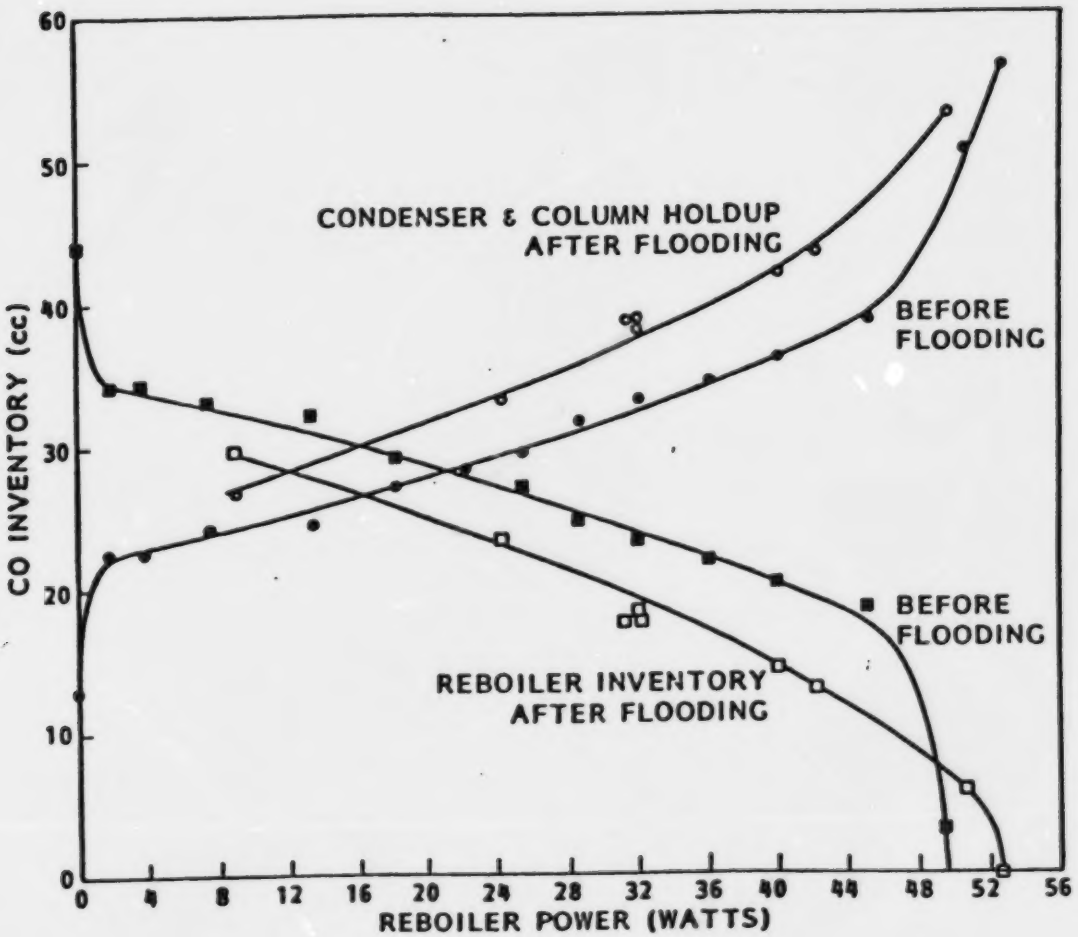

CO INVENTORY (cc)
REBOILER POWER (WATTS)
CONDENSER & COLUMN HOLDUP
AFTER FLOODING
BEFORE
FLOODING
BEFORE
FLOODING
REBOILER INVENTORY
AFTER FLOODING
0
10
20
30
40
50
60
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56

FIGURE 7

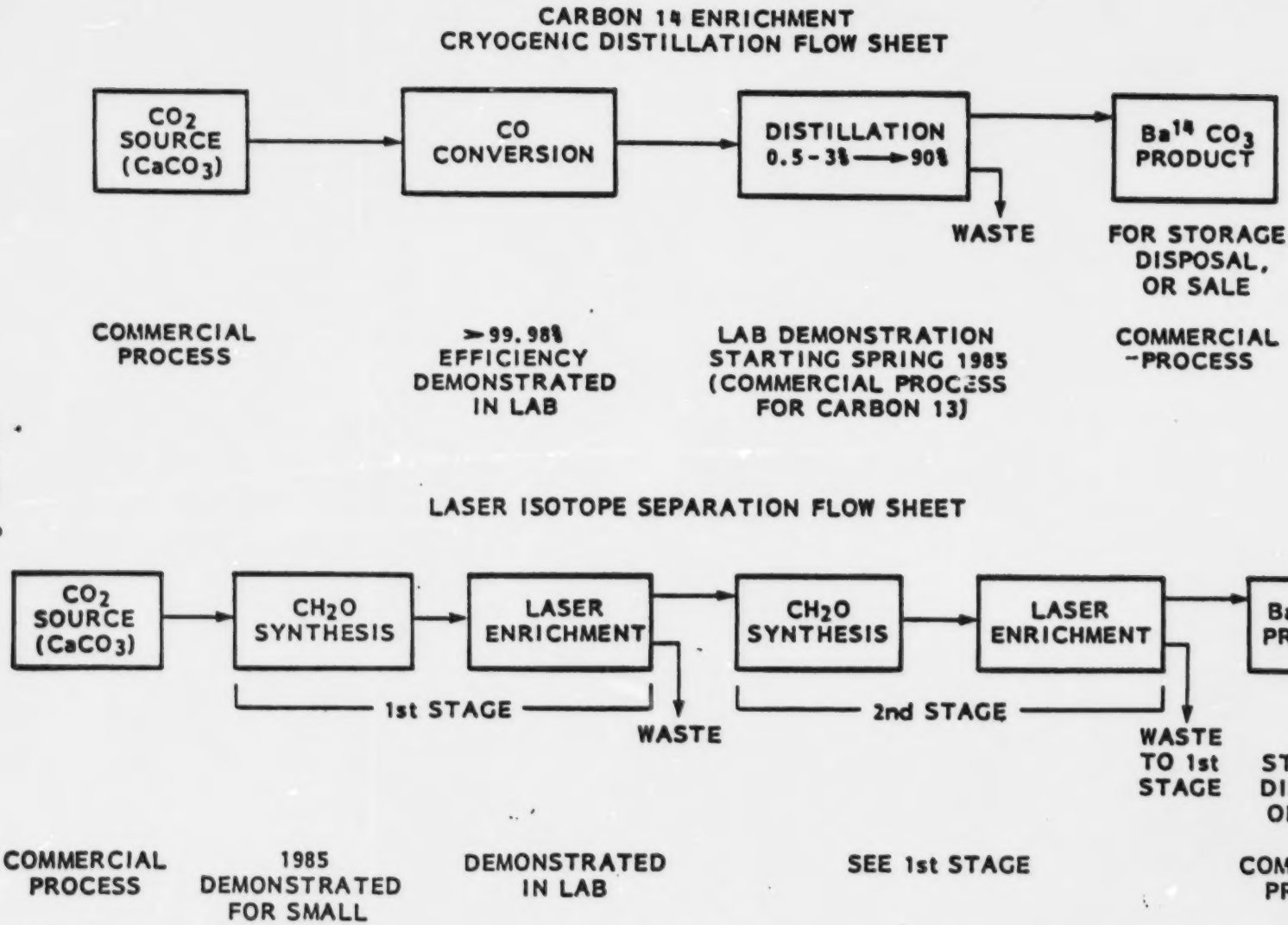

CARBON 14 ENRICHMENT
CRYOGENIC DISTILLATION FLOW SHEET
CO_2 SOURCE ($CaCO_3$)
CO CONVERSION
DISTILLATION 0.5-3% → 90%
$Ba^{14} CO_3$ PRODUCT
WASTE
FOR STORAGE, DISPOSAL, OR SALE
COMMERCIAL PROCESS
>99.98% EFFICIENCY DEMONSTRATED IN LAB
LAB DEMONSTRATION STARTING SPRING 1985 (COMMERCIAL PROCESS FOR CARBON 13)
COMMERCIAL -PROCESS
LASER ISOTOPE SEPARATION FLOW SHEET
CO_2 SOURCE ($CaCO_3$)
CH_2O SYNTHESIS
LASER ENRICHMENT
CH_2O SYNTHESIS
LASER ENRICHMENT
$Ba^{14} CO_3$ PRODUCT
1st STAGE
2nd STAGE
WASTE
WASTE TO 1st STAGE
FOR STORAGE, DISPOSAL, OR SALE
COMMERCIAL PROCESS
1985 DEMONSTRATED FOR SMALL QUANTITIES
DEMONSTRATED IN LAB
SEE 1st STAGE
COMMERCIAL PROCESS

FIGURE 8

TABLE 2

^{14}C PLANT CONCEPT

PRODUCTION	120 G/A ^{14}C
BOILUP	5 MB CO/A (9 B CO/MIN)
REBOILER ENERGY	36 W
COLUMN DIAM	17.2 MM
PACKING	HELIPAK A
HETP	2 - 3 CM
FEED CONCENTRATION	2% C^{14}
PROD CONCENTRATION	90%
PLATES	650
COLUMN HEIGHT	13 - 19 M
LN2 CONSUMPTION	28 L/DAY
(30% LOSSES)	10 000 L/A
HOLDUP	260 - 380 CC CO
	APPROX. 200 CI ^{14}C
	(could be reduced to 60 CI if bottom half of column reduced to 0.9 cm diam.)

TABLE 3

CARBON 14 PLANT COST (CRUDE ESTIMATE)

DESIGN AND CONSTRUCTION	200 000
INSTRUMENTATION	150 000
TOTAL	350 000
CAPITAL CHARGES 10%/A	35 000
SPACE 60 M^3 @ \$100/M^2/A	6 000
LN2 @ \$1/L	10 000
LABOUR (1 ENGINEER/MANAGER & 1 TECHNOLOGIST) \$/A	100 000
TOTAL \$/A	151 000

NOTE: LABOUR APPROX 2/3 OF COSTS
AUTOMATION IS CRITICAL

PRODUCTION	120 G
COST	\$1 250 /G
VALUE (wholesale)	\$15 000 /G
VALUE (retail)	\$250 000 /G

IT MAY BE POSSIBLE TO REDUCE LABOUR COSTS SUBSTANTIALLY THROUGH AUTOMATION

ISOTOPE SEPARATION BY ION EXCHANGE CHROMATOGRAPHY

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System Materials Branch
Atomic Energy of Canada Limited, Research Company
Chalk River Nuclear Laboratories
Chalk River, Ontario K0J 1J0

The feasibility of isotope separation by ion exchange chromatography has been successfully demonstrated for several elements including lithium, sodium, calcium and chlorine (1-4). Characteristics of this technique are reviewed in the following report with special reference to the Asahi Chemical Exchange process (ACEP), which has been developed to a pilot plant scale for the enrichment of uranium-235.

Ion exchange chromatography is one example of the chemical exchange methods that have been suggested for isotope separation on an industrial scale. All such methods are based on equilibrium isotope effects where the equilibrium constant for the exchange reaction shown in Figure 1 is not equal to 1.0. In this generalized equation, A and B represent two distinct phases, which in ion exchange chromatography consist of a mobile liquid phase and a stationary resin phase. Some of the advantages and disadvantages of chemical exchange methods are listed in Figure 2 and the properties of an ideal chemical exchange system for isotope separation are presented in Figure 3.

Most ion exchange resins are made by copolymerization of styrene and divinylbenzene which results in a cross-linked network to which ionized or ionizable groups (denoted by R in Figure 4) can be attached. The functional groups ionize to give an ion fixed to the polymer matrix and a counter ion in the liquid phase which can be replaced by an ion of the same charge (5).

The exchange rate of ions in the chromatographic column is the sum of three separate processes (listed in Figure 5). Film diffusion refers to diffusion of the solute ion from the solution through the relatively stagnant solvent layer at the surface of the resin particle and of the counter ion to the solution from the particle surface. Film diffusion is an important factor in the observed exchange rate under conditions of high fixed ion concentration, low cross-linking, small particle size, dilute solution, low temperature and poor agitation. Particle diffusion describes the movement of the solute ion through the resin to the exchange site and of the counter ion out of the resin. Particle diffusion, which is usually the rate-controlling step in ion exchange columns, is strongly dependent on the degree of cross-linking and size of particle. The third factor, replacement of the counter ion by the solute ion at the exchange site, is generally rapid but may be a limiting step for some chelating exchange resins.

The three basic types of chromatographic experiments are shown in Figure 6. A breakthrough or frontal process occurs when the solute is simply washed down the column and isotope exchange or reflux occurs at the leading edge. Reverse breakthrough describes the process where the resin is fully loaded with solute ions and then eluted so that reflux occurs at the rear boundary. In displacement chromatography, the solute is loaded onto the top of the resin bed

and eluted as a band in which reflux takes place at both the front and rear boundaries. Isotope separation by ion exchange chromatography is usually demonstrated by a breakthrough experiment and large scale processes are based on continuous band elution.

A breakthrough procedure was used by Jepson and Stockey (6) to demonstrate calcium isotope enrichment by ion exchange chromatography. The experimental data obtained by passing an aqueous solution of calcium hydroxide over a sulphonic acid resin are illustrated in Figure 7. Although the observed separation coefficients for calcium are relatively large in these experiments, the low solubility (0.017 mol/L) of calcium hydroxide makes this system unsuitable for use on a commercial scale. The equilibria describing the exchange process are shown in Figure 8. Equations 1, 2 and 4 are parallel reactions and equations 1 and 3 are consecutive reactions, the sum of which yields 4. Separation coefficients for Equations 1, 3 and 4 were calculated using the experimentally measured value of ϵ_{obs} and a published value of ϵ_2. Since variations of pH, temperature, solute concentration, etc. can affect each of these separation coefficients to a different extent, optimization of conditions for an industrial-scale process is very difficult. In fact, large scale isotope separation by ion exchange chromatography has been reported for only uranium. Some of the parameters associated with the choice of solute, solvent, resin, and operating conditions required to develop such a process are listed in Figure 9.

The Asahi Chemical Exchange Process (ACEP) was developed in Japan for the enrichment of uranium-235. ACEP is based on redox ion exchange chromatography using a strongly basic anion exchange resin and a U(VI)/U(IV) redox couple as shown schematically in Figure 10 (7). Initially the column is loaded with a salt of iron (III). As a solution of uranium salts is added, any U(IV) present is oxidized to form U(VI) which is efficiently adsorbed by the resin. The uranium band is eluted with a solution of titanium (III) which reduces the U(VI) bound to the resin and returns U(IV) to the mobile phase. The solution containing U(IV) passes down the column until it reaches the front of the band where U(IV) is again oxidized by iron (III) bound to the resin. Repetition of this cycle as the band travels down the column represents a countercurrent exchange system. Key factors in demonstrating the viability of this process were the development of a new ion exchange resin with fast adsorption/desorption rates and the use of redox catalysts which accelerate the U(IV)/U(VI) isotope exchange reactions. As a result of these discoveries, the overall reaction rate was improved by a factor of 10^4 (7).

For continuous operation, a set of four columns can be arranged to form a module as shown in Figure 11 (8). Three columns are used to contain the uranium band and the fourth is reserved as a standing column. Uranium-235 is enriched at the rear (reducing) boundary and depleted at the front (oxidizing) boundary of the uranium band. The deactivated redox agents are regenerated in two auxiliary columns. In the oxidation column, the oxidizing agent is reactivated by passing oxygen gas through the solution. In the reduction column, the reducing agent is regenerated by reaction with hydrogen gas over a granular hydrogenation catalyst. Periodic withdrawals of enriched and depleted materials with compensating additions of feed uranium are made by means of the multiselector valves.

Fujine et al. (7) explored the sensitivity of this system to various operating parameters using theories previously developed for a square cascade and assuming the base conditions listed in Figure 12. Using this reference case, they calculated the isotope concentration profile across the adsorption band as a function of time. Their results, shown in Figure 13, predicted that uranium-235 could be enriched to 3.0% in approximately 3.8 months and that a tails concentration of 0.1% is readily achieved in a column four metres long. They also found that a slight increase in the separation factor would significantly reduce the lead time and increase the separa-

tive power of the system. Increasing the band length (ie, the number of theoretical stages) has similar effects on lead time and separative power but such changes also affect the costs of plant construction and operation. ACEP is unsuitable for the economical production of highly enriched uranium because of the excessively long lead time required (10 years) as well as criticality control problems associated with high concentrations of uranium-235 in aqueous solutions.

These theoretical calculations were used to determine optimum parameters for the design and construction of a bench-scale plant (9). After four months of continuous operation of the plant, a small amount of 3%-enriched uranium was recovered. Excellent agreement between theoretical calculations and experimental results was achieved as illustrated in Figure 14. Thus, ACEP has been established as a feasible method for uranium enrichment.

Some of the advantages of ACEP compared to other separative techniques in general and to the French CHEMEX process in particular are listed in Figure 15. (The latter is the only other chemical exchange process for uranium enrichment that has been developed to a commercial scale). These features make ACEP technology attractive for the production of low-enriched uranium in Canada.

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FIGURE 1

Equilibrium Isotope Effects

$$X_{(A)} + X'_{(B)} \rightleftharpoons X_{(B)} + X'_{(A)}$$

$$K_{eq} = \frac{[X_{(B)}]\,[X'_{(A)}]}{[X_{(A)}]\,[X'_{(B)}]} \neq 1.00000\ldots\ldots$$

FIGURE 2

Chemical Exchange Methods

Advantages

- low energy consumption
- well known large-scale technology
- used for a wide range of elements

Disadvantages

- difficult on a small scale
- unique system for each element
- no middle isotopes

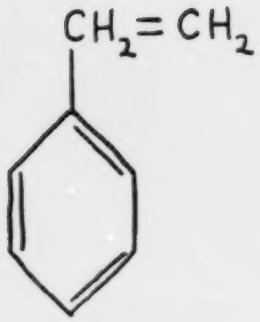
FIGURE 3

Properties of an Ideal System

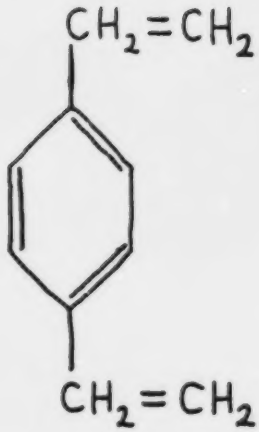
- Stable phases
- Rapid isotopic exchange
- Large isotopic K_{eq}
- Simple solute conversion
- Solute dilution
- Ease of construction and operation

FIGURE 4

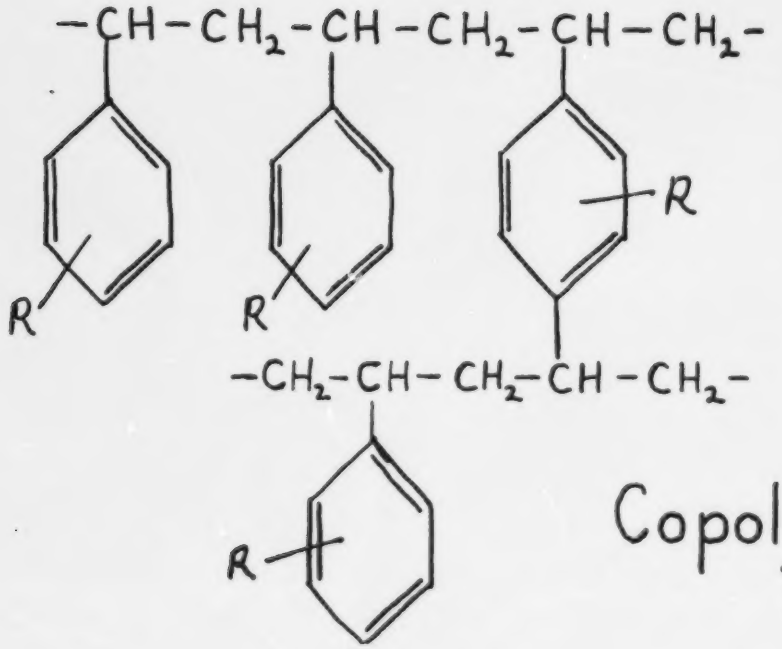
Ion Exchange Resins



Styrene



Divinylbenzene



Copolymer

R
SO_3H
COOH
OH
NH_2
$N(CH_3)_2$

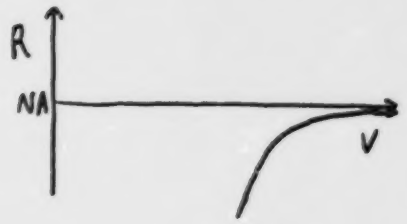
FIGURE 5

Rate of Exchange

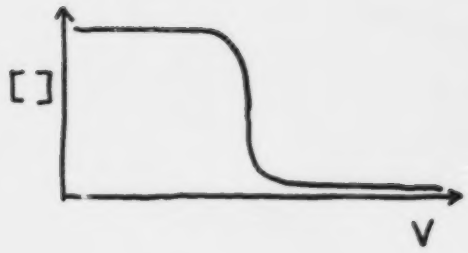
- Film diffusion
- Particle diffusion
- Ion replacement at exchange site.

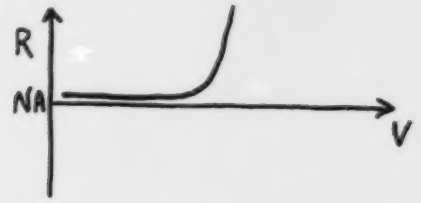
FIGURE 6

Ion Exchange Chromatography

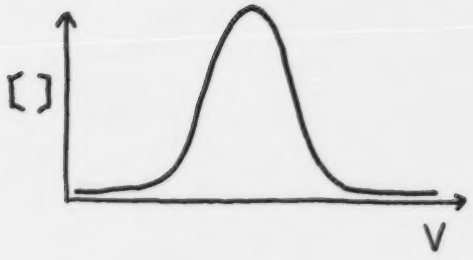


Breakthrough



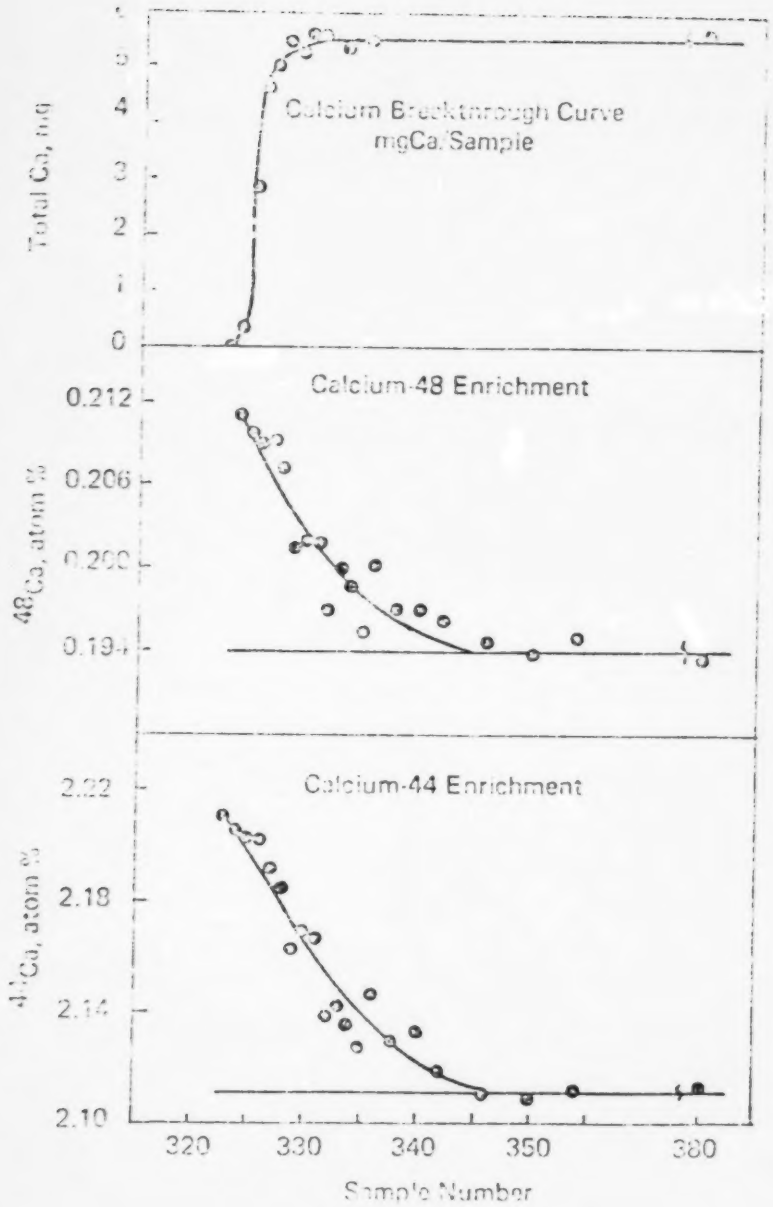


Inverse Breakthrough



Displacement

FIGURE 7



Calcium breakthrough curve and isotope enrichment.

FIGURE 8

Calcium Isotope Separation

ϵ (44/40)

(1) $^{40}Ca^{2+}_{(aq)} + {}^{44}Ca(SO_3R)_{2\,(res)} \rightleftharpoons {}^{44}Ca^{2+}_{(aq)} + {}^{40}Ca(SO_3R)_{2\,(res)}$ 8.5×10^{-4}

(2) $^{40}Ca(OH)^{+}_{(aq)} + {}^{44}Ca(SO_3R)_{2\,(res)} \rightleftharpoons {}^{44}Ca(OH)^{+}_{(aq)} + {}^{40}Ca(SO_3R)_{2(res)}$ 7.5×10^{-4}

(3) $^{44}Ca^{2+}_{(aq)} + {}^{40}Ca(OH)_{2\,(aq)} \rightleftharpoons {}^{40}Ca^{2+}_{(aq)} + {}^{44}Ca(OH)_{2\,(aq)}$ 13×10^{-4}

(4) $^{40}Ca(OH)_{2\,(aq)} + {}^{44}Ca(SO_3R)_{2\,(res)} \rightleftharpoons {}^{44}Ca(OH)_{2\,(aq)} + {}^{40}Ca(SO_3R)_{2(res)}$ 15×10^{-4}

$\epsilon_{obs} = 11 \times 10^{-4}$

FIGURE 9

Important Parameters

- Solute - oxidation state, chemical form,
  - counterion, concentration
- Solvent - for resin loading, elution
  - for solute reflux, buffers
- Resin - degree of cross-linking, porosity
  - choice of functional group
  - mesh size, capacity, loading
- Process - temperature, flow rate
  - band length
  - enrichment/depletion targets

FIGURE 10

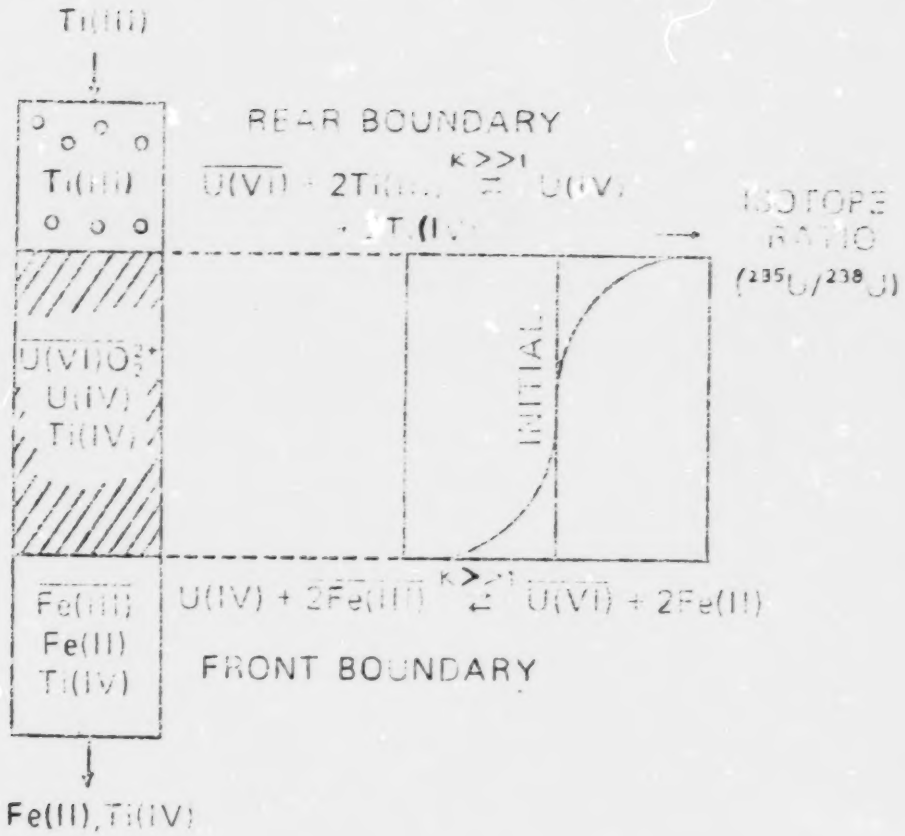

Ti(III)
Ti(III)
REAR BOUNDARY
U(VI) + 2Ti(III) K>>1 U(IV) + 2Ti(IV)
ISOTOPE RATIO ($^{235}U/^{238}U$)
INITIAL
U(VI)O$_2^{2+}$
U(IV)
Ti(IV)
Fe(III)
Fe(II)
Ti(IV)
U(IV) + 2Fe(III) K<<1 U(VI) + 2Fe(II)
FRONT BOUNDARY
Fe(II), Ti(IV)

FIGURE 11

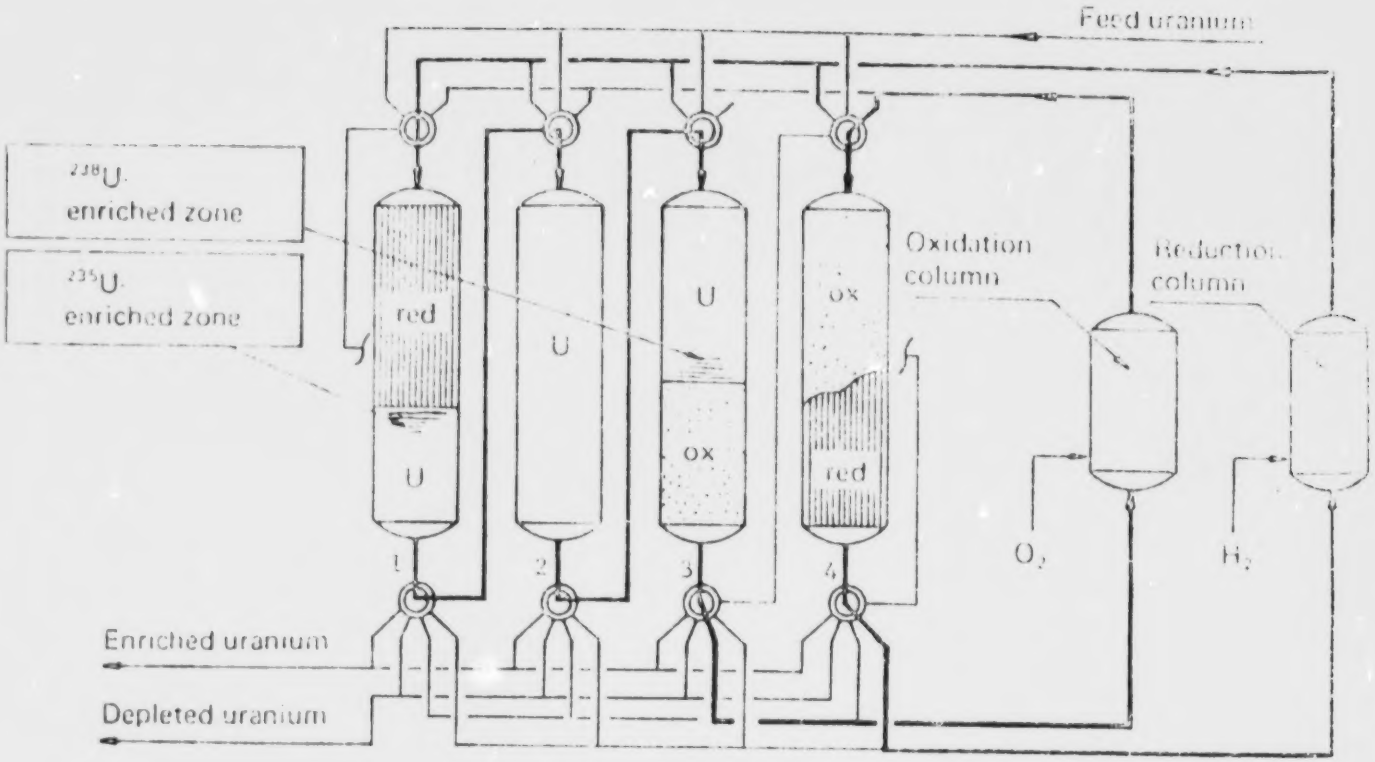

Feed uranium
^{238}U enriched zone
^{235}U enriched zone
red
U
U
U
ox
ox
red
Oxidation column
Reduction column
O_2
H_2
1
2
3
4
Enriched uranium
Depleted uranium

FIGURE 12

Base Factors for Reference Case

Isotope Separation Factor	1.0010
Band Flow Rate	1 m/hour
HETP	0.8 mm
Ion Exchange Capacity	0.25 mol/L
Uranium Concentration	0.15 M
Void Fraction of Resin Bed	0.35
Total Stage Number	5000
Column Diameter	1 m
Product Withdrawal Interval	6.9 d

FIGURE 13

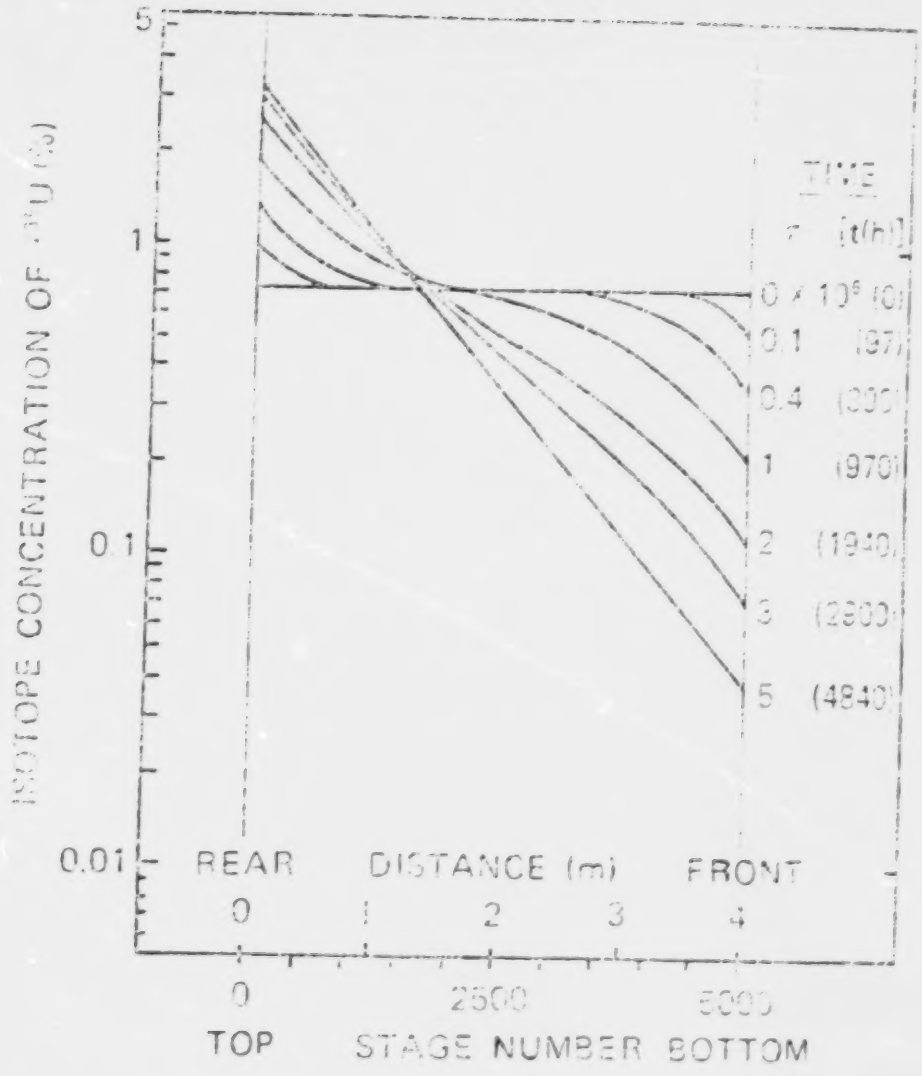

5
1
0.1
0.01
TIME
τ (t/h)
0.4 (300)
1 (970)
2 (1940)
3 (2800)
5 (4840)
REAR
DISTANCE (m)
FRONT
0
2
3
4
0
2500
TOP
STAGE NUMBER
BOTTOM

FIGURE 14

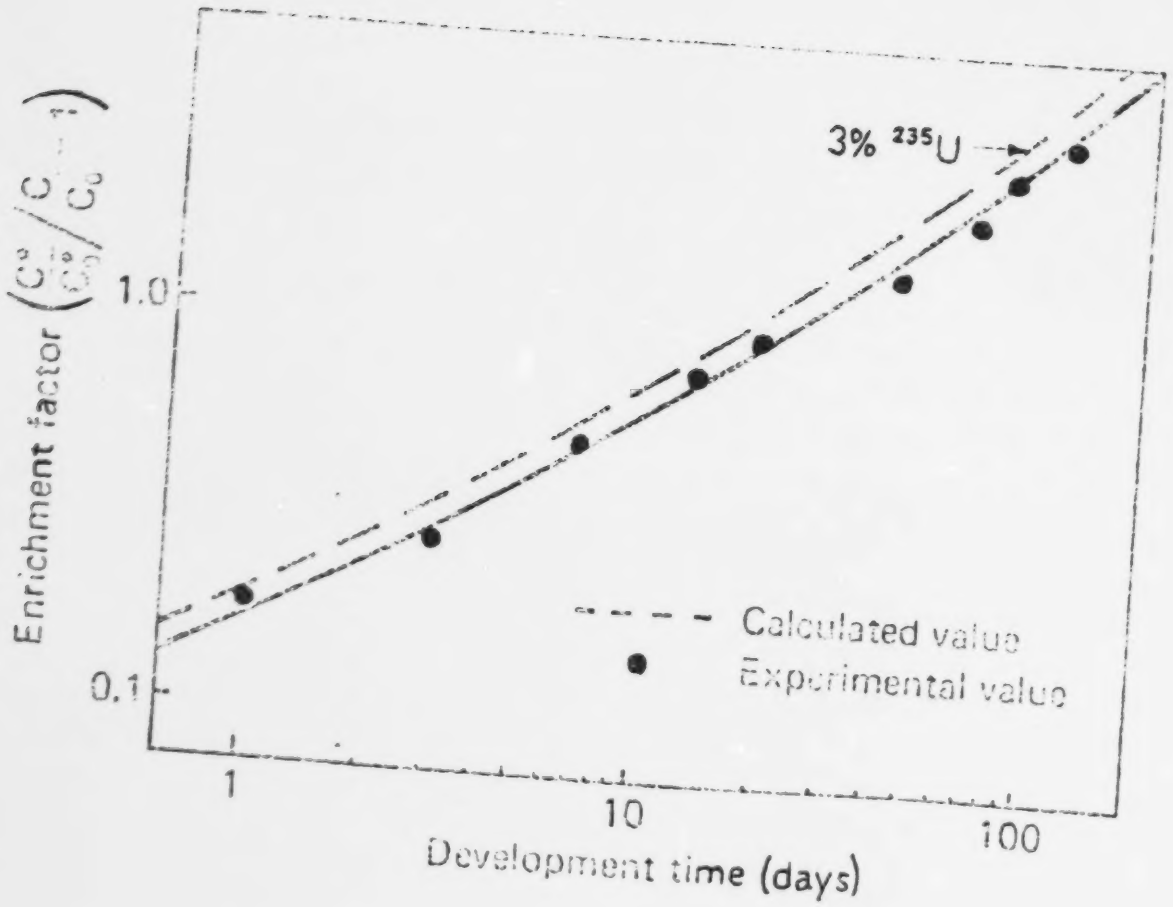

3% ^{235}U
1.0
0.1
Calculated value
Experimental value
1
10
100
Development time (days)

FIGURE 15

ACEP Advantages

- Modular
- No cascade control needed
- Simple equipment
- Few moving parts
- Proliferation proof - time constant
  - criticality

Compare to CHEMEX

- lower U inventory
- fewer operations
- longer plant life
- lower energy consumption

FACTORS IN THE SELECTION OF WORKING MOLECULES FOR LASER ISOTOPE SEPARATION

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Chalk River, Ontario K0J 1J0

(Summary by H.D. Morrison, Ontario Hydro Research Division)

Laser isotope separation (LIS) by multiphoton decomposition (MPD) consists of a sequence of processes whose operation depends on the choice of working molecule and the isotope of interest. To be specific, this discussion is confined to hydrogen isotope separation, but the principles apply to any element. For deuterium separation, the source of deuterium is either HDO or CH_3D. There are four processes:

(1) chemical process to transfer the isotope to a molecule suitable for LIS;
(2) laser excitation of selected isotope to produce secondary species (stable molecules are best);
(3) capture of selected secondary species;
(4) transformation of secondary species to usable product.

There are several factors involved in the selection of the working molecule to undergo these processes:

(1) chemical and physical properties - as they affect cost, exchange and hydrolysis, volatility, toxicity, reactivity, photochemistry and the nature of the product;
(2) selectivity - optical selectivity S, measured as the ratio of absorption cross-sections, should be in the range of 100 to 1000, with a photon efficiency of 1-10%;
(3) decomposition probability as a function of fluence - low fluence is desirable to avoid optical damage;
(4) optical properties - frequency region, non-linear absorption and refractive index effects, e.g. CF_3H exhibits self-focusing;
(5) selection of laser;
(6) cell design;
(7) other factors.

Other factors include improving the suitability of the working molecule, which requires a better understanding of MPD:

(1) multi-colour - less photon waste, e.g. CDF_3, $CTCl_3$, OsO_4, UF_6;
(2) collisions - presence or absence, e.g. in freons;
(3) intensity dependence - as in CF_3I;
(4) electric and magnetic fields - as in CDF_3;
(5) added groups to chromophores - OH containing molecules;
(6) better understanding of multiphoton absorption.

Consider some of these factors for several specific molecules for deuterium or tritium separation:

(1) alcohols - rapid exchange;

(2) CDF_3 and CTF_3 - slow exchange, high fluence, non-linear index effects, the product is HF;
(3) CCl_3T - high selectivity for T, low for D, better exchange and lower fluence than for CTF_3, the product is HCl;
(4) $CHDCl_2$ and various others similar such as $CDClF_2$ - exchange probably difficult, high selectivity may be possible;
(5) $(CF_3)_2CFT$ - MPD fluence is 10% of CDF_3, selectivity decreases with pressure, hydrolysis may be a problem, high selectivity may be possible with a short pulse (2 ns) $^{13}CO_2$ laser.

A review article on this topic is available:

R.D. McAlpine and D.K. Evans, "Laser isotope separation by the selective multiphoton decomposition process," Adv. Chem. Phys. 60, 31-98 (1985).

ELECTRICAL ANHARMONICITY AND COHERENT MULTIPHOTON EXCITATION IN A LASER + DC FIELD

Gerald F. Thomas
Chemical Research Department
Ontario Hydro Research Division

The effects of electrical anharmonicity on the coherent multiphoton excitation of a molecule in a laser + dc field are described. The theory is used to rationalize the observed enhancement in the IRMPD of CF_3D in the presence of a static field as reported by van den Bergh and co-workers (J. Chem. Phys. 79, 4924 (1983)). More complete details are available in:

G.F. Thomas, "Electrical anharmonicity and coherent multiphoton excitation in a laser + dc field", J. Chem. Phys., to be submitted (1985).

G.F. Thomas, "Effects of permanent dipole moments on the collision-free interaction of a two-level system with a laser and a static electric field", Phys. Rev. A, accepted for publication (1985).

G.F. Thomas, "Dipole interaction of a multilevel system with a continuous-wave or Gaussian-pulsed laser", Phys. Rev. A, in press (1985).

G.F. Thomas, "Validity of the Rosen-Zener conjecture for Gaussian-modulated pulses", Phys. Rev. A 27, 2744 (1983).

G.F. Thomas, "The enhancement of intense laser induced multiphoton processes by a static electric field", J. Chem. Phys. 79, 4912 (1983).

G.F. Thomas, "Modification of the Rabi flopping frequency in the presence of a static electric field", Opt. Commun. 47, 196 (1983).

G.F. Thomas and W.J. Meath, "An algorithm for the evaluation of induced transition probabilities for non-sinusoidal and sinusoidal applied fields with an application to Gaussian pulses", J. Phys. B16, 951 (1983).

G.F. Thomas and W.J. Meath, "Multiphoton vibrational resonances, with modulation effects, using HeXe, NeAr and NeXe as models", Molec. Phys. 46, 743 (1982).

G.F. Thomas and W.J. Meath, "On the time dependence of a degenerate two-level system interacting with a pulse of radiation", Phys. Lett. A70, 396 (1979).

WORK AT WESTINGHOUSE ON ZIRCONIUM ISOTOPE SEPARATION TECHNOLOGY

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Westinghouse Research & Development
1310 Benlah Road
Pittsburgh, PA 15235

(Summary by H.D. Morrison, Ontario Hydro Research Division)

The program of zirconium isotope separation work at Westinghouse was divided into three areas. The first was molecular laser isotope separation (MLIS) under the direction of Jack Feichtner, the second was photo-assisted solvent extraction (PHASE) directed by S.H. Peterson, and the third was solvent extraction (ISUSE) directed by Ed Lahoda. The first slide provides a summary of the economic factors in the three approaches, listing the minimum alpha separation factors required for commercial feasibility, the expected capital costs and the incremental product cost. The numbers in parentheses in the second column are the real alpha separation factors obtained in the experiments. This slide shows that ISUSE not only has the cheapest costs, but also is the only process to exceed the minimum alpha required for economic viability. In March 1985, soon after technical feasibility was demonstrated, the zirconium isotope separation program at Westinghouse was terminated due to general tightness of funds in Westinghouse's Nuclear Fuels Division. A summary of the main points from the remaining slides follows.

The objective of isotopic separation of zirconium is determined by the process used and can be viewed as approaching one of two extremes: one is 100% enriched 90-Zr (MLIS), and the other is 100% removal of 91-Zr (PHASE and ISUSE). The estimated fuel cost savings are slightly greater for enriched 90-Zr than for the metal depleted in 91-Zr because of the contribution to the thermal neutron absorption cross-section by the other even isotopes. Cost savings also depend on the intended application. PWR and BWR systems have much lower potential savings than CANDU reactors. For comparison purposes, the assessments of economic viability for the three processes were based on once-through utilization of denatured zirconium in PWR and BWR fuel cladding with no reprocessing.

The economics of the MLIS process are based on employing CO_2 lasers, the least expensive source of photons, in a single stage process. With these assumptions a minimum separation factor of 15 is required to provide reasonable capital and incremental costs. The highest alpha produced by a MLIS process was 1.9 (^{90}Zr-^{91}Zr) obtained by CO_2 laser dissociation of a molecular beam of zirconium t-amyloxide. This separation factor is too small for economic viability based on PWR fuel cladding, but could be attractive for CANDU reactor calandria if no other process is available.

The PHASE and ISUSE processes are based on counter-current flow of aqueous and organic solvents. The PHASE method employs light to enhance the separation factor by selectively exciting and extracting 91-Zr. A larger separation factor results in smaller plant size than the ISUSE method but design is difficult since too much light power boils the solvents. Zirconium isotope selectivity was observed in samples utilizing diketone and amine based extractants, and a maximum separation factor of 1.4 was obtained. An economic analysis shows that this process is only marginally viable for PWR systems.

The most successful results were obtained with ISUSE, a conventional solvent extraction process that only relies on differences in molecular weight for separation. Thus the aim of this process is to throw away 90-Zr and 91-Zr and retain the three other isotopes. Tests began with single-stage shakeout of 72 different systems, followed by ten-stage shakeout on 19 of those systems of which 5 had a 94/91 alpha greater than 1.006. The final series of 15 tests examined four types of columns and produced 94/91 alpha's of 1.036 per column. Thus, Zr separation with solvent extraction is technically feasible and economically viable. Final product costs of $23 to $35 per pound of enriched 92-Zr, 94-Zr and 96-Zr are likely with capital costs between $15 and $30 million for a plant producing 950,000 lb/yr of $ZrCl_4$.

ZIRCONIUM ISOTOPE SEPARATION

Molecular Laser (MLIS)

Photo-Assisted Solvent Extraction (PHASE)

Solvent Extraction (SX)

E. J. Lahoda

S. H. Peterson

J. D. Feichtner

Westinghouse Research & Development Center

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SUMMARY

	α	Capital Cost (Millions of $)	Incremental Zr TREX Product Cost ($/pound)
MLIS	15-20 (1.5)	60-75	40-60
PHASE	1.08-1.12 (1.05)	35-50	40-50
ISUSE	1.004 (1.008)	15-30	20-35

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ECONOMICS OF ISOTOPIC SEPARATION OF ZIRCONIUM

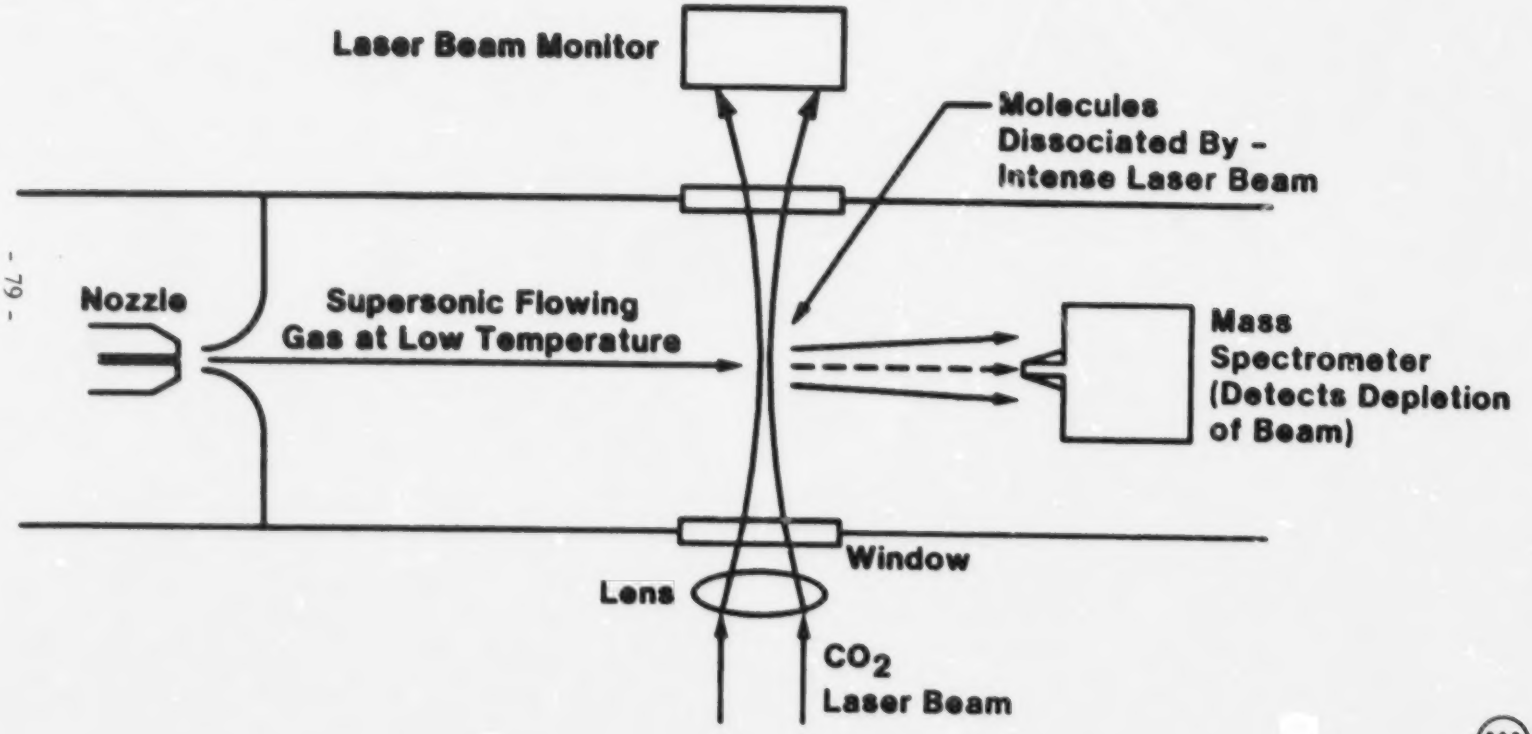
Isotope	Abundance (%)	Absorption Cross Sections (Barns) Fast	Thermal
Zr-90	51.5	.016	.033
Zr-91	11.2	.160	.537
Zr-92	17.1	.033	.086
Zr-94	17.4	.020	.030
Zr-96	2.8	.200	.013
Avg.		.047	.097

Isotopic Separation	Fuel Cost Gross Savings* PWR	BWR	CANDU
100% Removal of 91-Zr	2.4%	5.3%	7.9%
Use of 100% Enriched 90-Zr	3.3%	7.4%	11%

*Gross savings calculated for 100% enrichment; net savings will peak at about 90% enrichment when enrichment cost is considered. Savings in % increase in burnup

88-99

EXPERIMENTAL CONFIGURATION FOR MEASURING CO_2 LASER MULTIPHOTON DISSOCIATION IN SUPERSONIC MOLECULAR FLOWS



88-99

SUMMARY STATUS WESTINGHOUSE ZIRCONIUM MLIS EXPERIMENTS

- Molecular Beam Measurements Of CO_2 Laser Dissociation Of Zirconium t-Amyloxide In Supersonic Beam.
- Largest Observed α (^{90}Zr-^{91}Zr)=1.9

  CUT=25%
  Laser Wavenumber=993.0cm^{-1}
  Fluence=5J/cm^2

- Large Zr/Hf Selectivities Also Observed

ECONOMICS OF Zr MLIS

Assumptions

- Once-through utilization of enriched Zr in fuel cycle, for fuel cladding only. No reuse of enriched Zr
- Product 89 w/o ^{90}Zr, 1 w/o ^{91}Zr
- $Zr(BD_4)_4$ carrier compound
- CO_2 Laser multiphoton process
  - Maximum 22 photons/reacted molecule
  - Minimum photon utilization 50%
  - Minimum laser efficiency 10%
  - Maximum laser capital cost $100/watt
- Single stage process
- 600,000 lb./yr. Zr production

Conclusion

- α = 15 to 20 required to provide a single stage process with reasonable capital cost and incremental cost of Zr TREX product

Zr MLIS PLANT COST FACTORS (950,000 lbs/yr of $ZrCl_4$)

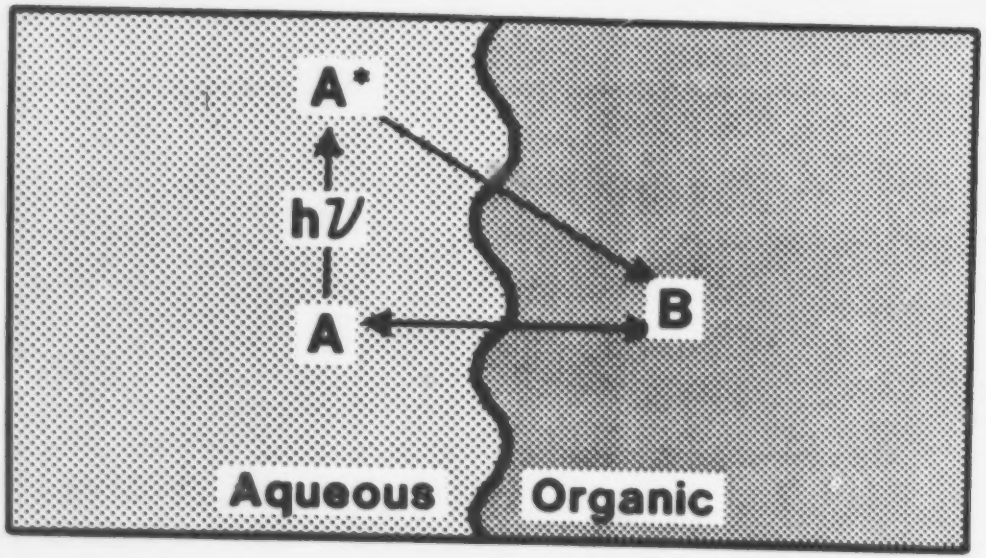
Separation Factor, α	Plant Capital Cost, $M	Incremental Cost of Zr TREX, $/lb.
10	117	110
15	73	56
20	63	42

CONCLUSIONS

Zr isotopic selectivity has been observed in molecular beam measurements of CO_2 laser dissociation of Zirconium t-Amyloxide, however, separation factors measured are not yet large enough for economic viability of a plant based on this effect

This conclusion is based on once-through utilization of the enriched Zr in PWR and BWR fuel cladding, with no reprocessing. Application to CANDU reactor calandria tubes or to fuel cycles involving reprocessing would relax the requirement for such a high separation factor

IDEAL PHASE SYSTEM

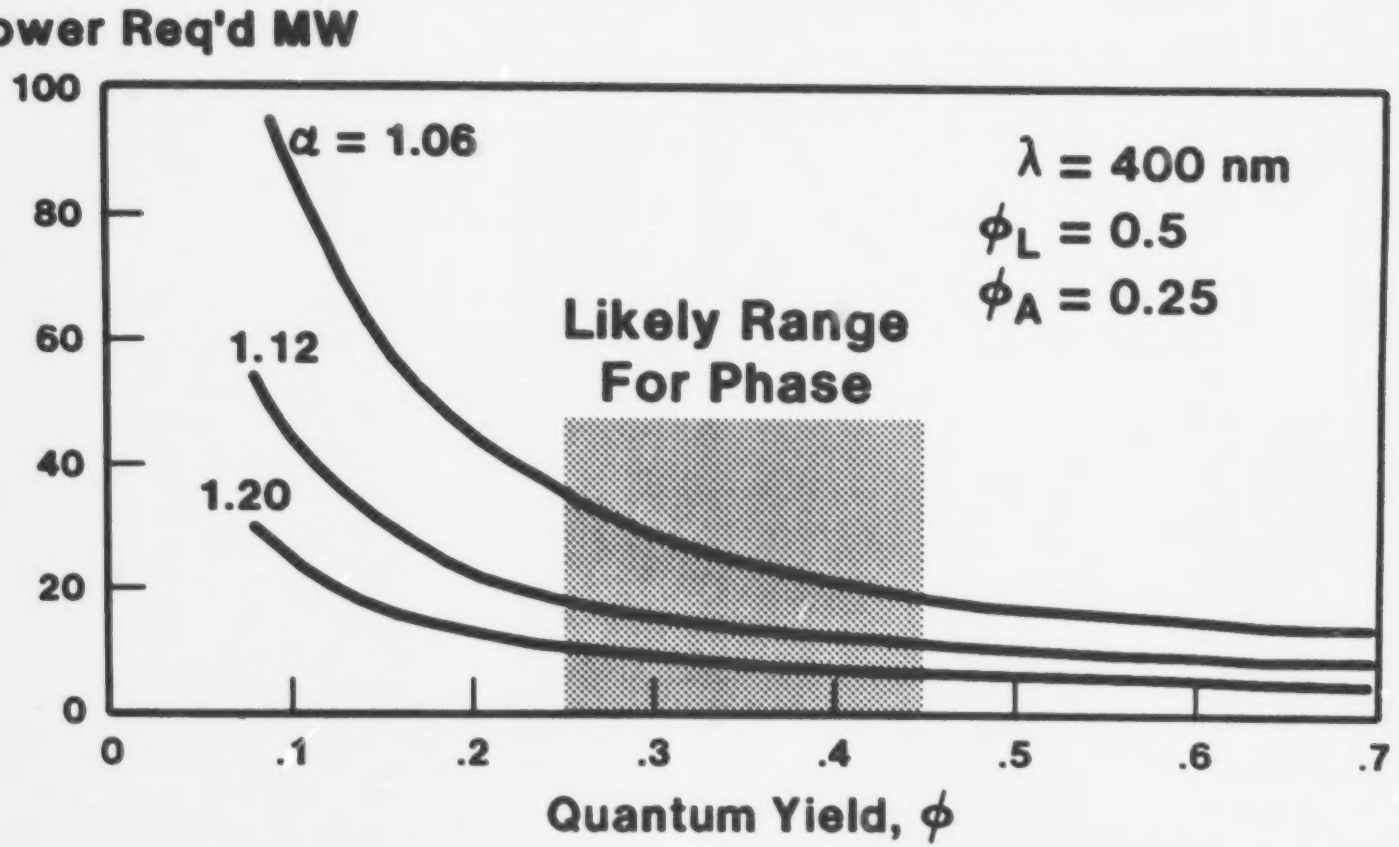


Equilibrium $K_D = [A] / [B]$

Excitation $X^*_O(A) = \dfrac{KX_O(A)}{KX_O(A)\ X_O(A) + 1}$

$K = \tau_O / \tau_e$

ELECTRICAL POWER REQUIREMENTS FO.
1 MILLION LBS $ZrCl_4$ /YR "PHASE" PLANT WITH
<1% ^{91}Zr, AT OVERALL α = 17.5



SINGLE STAGE PHASE ^{91}Zr SEPARATION FACTORS FOR SELECTED SOLVENT PAIRS

Aqueous \ Organic	β -diketone - Xylene	Amine - Kerosene
$Zr(SO_4)_2$ H_2SO_4	1.023	1.009
$ZrOCl_2$ HCl	1.040	1.007
$Zr(NO_3)_2$ HNO_3	1.020	1.010
$Zr(ClO_4)_4$ $HClO_4$	1.015	---
$ZrOCl_2$ Oxalic Acid	1.018	1.008

PRODUCT COSTS ESTIMATED FOR PHASE PRO SS
ANNUAL PRODUCTION 950,000 lb $ZrCl_4$
OVERALL PROCESS α = 17.5

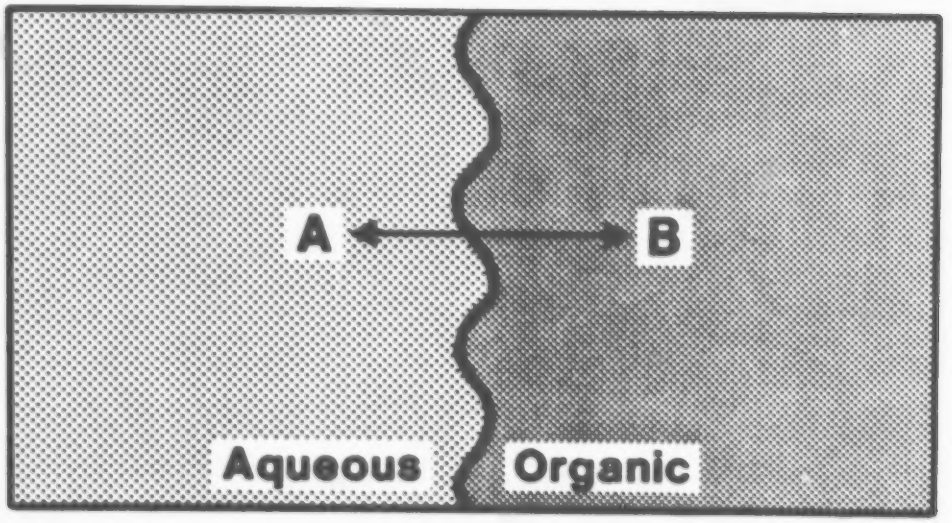
α_s	# Stages	Capital Cost, $M	Product Cost $/lb (Zr)
1.05	58	58.3	78.6
1.08	37	45.7	55.1
1.10	30	41.5	47.2
1.12	25	38.5	41.6
1.20	15	32.5	30.3

PHASE CONCLUSIONS

1. Zr isotope selectivity was observed in samples utilizing diketone and amine based extractants. α's up to 1.04 per stage were found

2. Economic viability is marginal for PWR reactors with capital costs estimated at $35-50 million for a 950,000 lb./yr. of ZrCly plant and incremental Zr TREX costs of $40-50/lb.

SOLVENT EXTRACTION



Equilibrium K_D = [A] / [B] = 1.001 to 1.01

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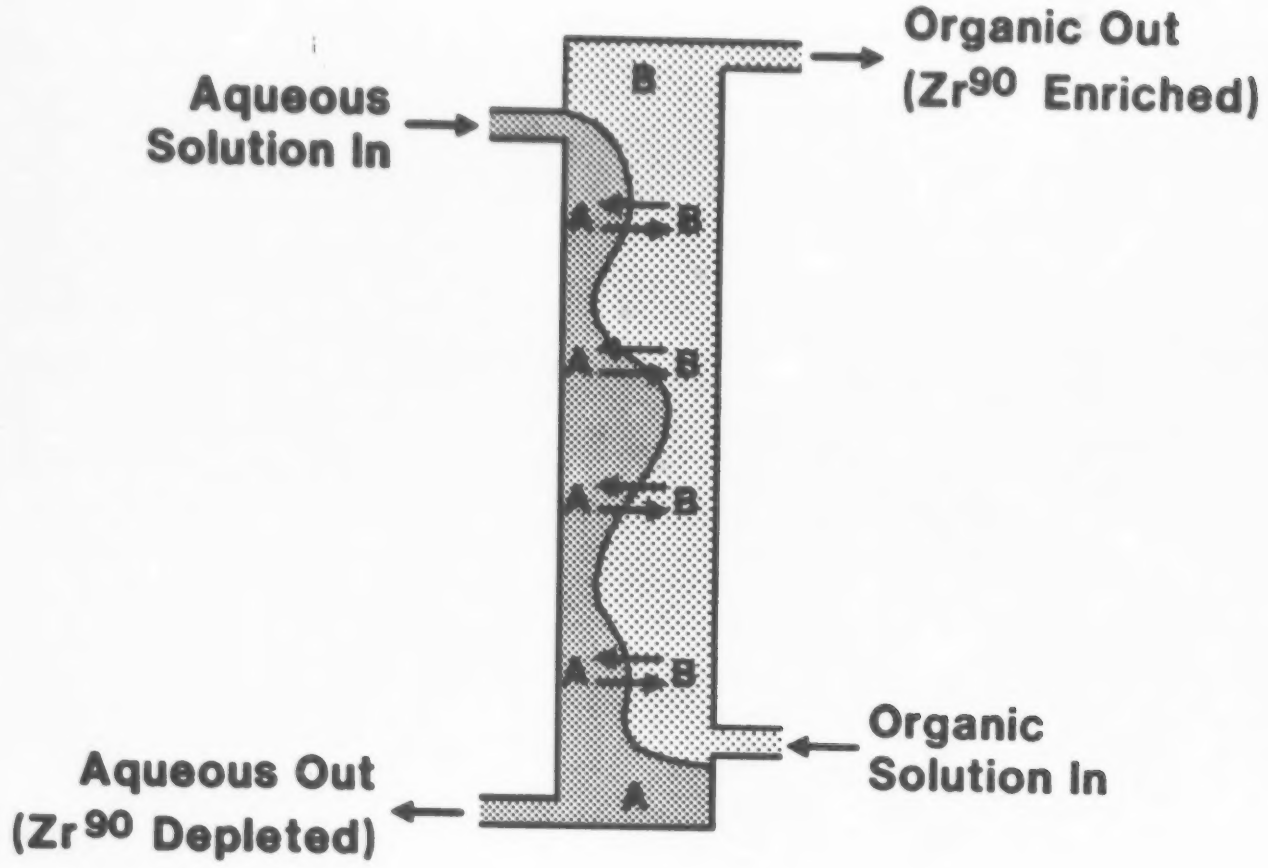
SOLVENT EXTRACTION COLUMN



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ALTERNATE PRODUCTS

Zr Isotope	σ	Atoms
90	.033	51.46
91	.537	11.23
92	.086	17.11
94	.030	17.40
96	.013	2.80
Zirconium	.118	-

Product 1

Component	Atom %	Weighted (σ)
Zr 90	99	.033
Zr 91	1	.005
Total	100	.038

Product 2

Zr 92	17.8	.016
Zr 94	70.8	.021
Zr 96	11.4	.001
Total	100.0	.038

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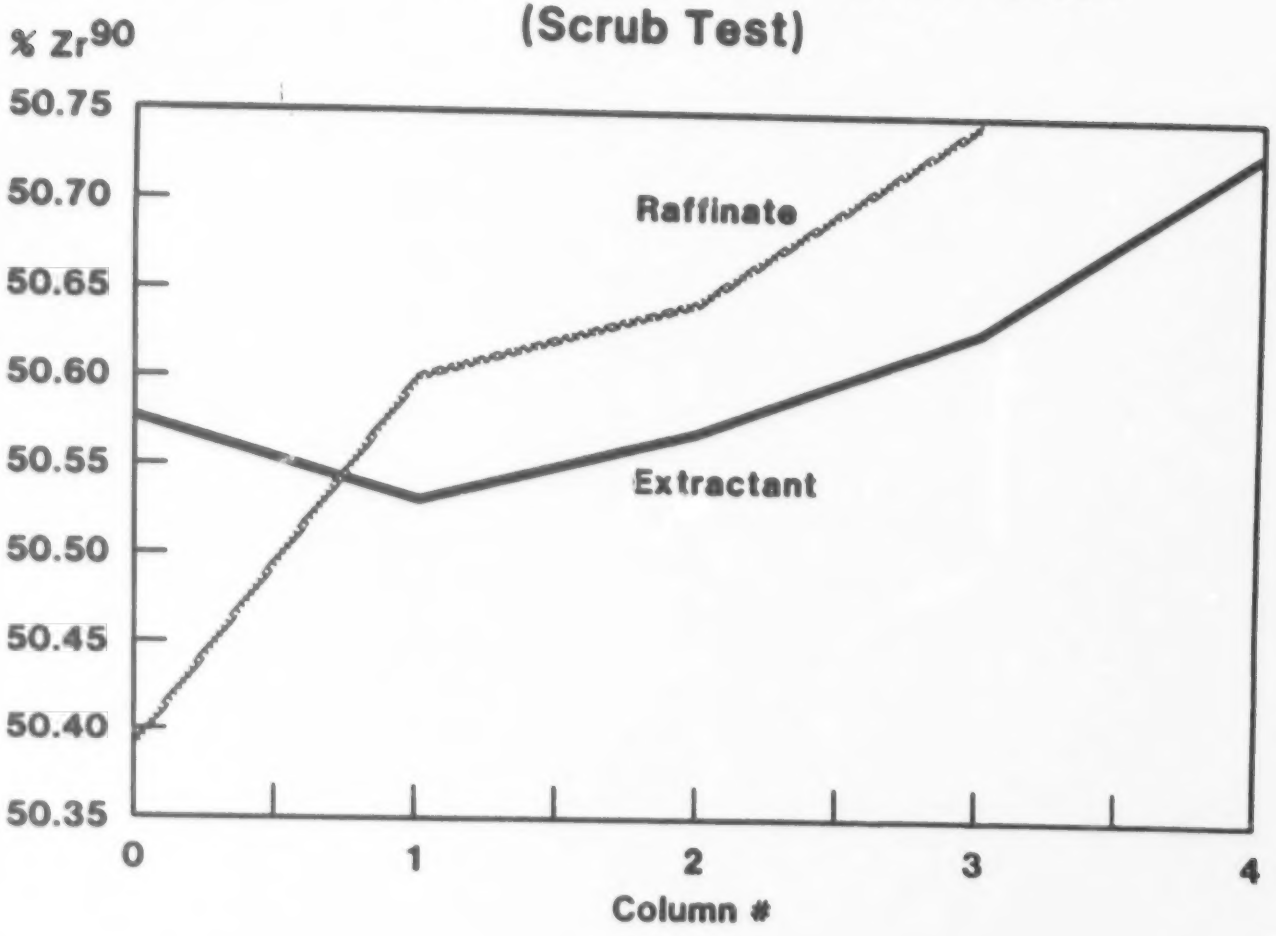
PROOF OF PRINCIPLE RESULTS

1. Single stage shakeouts - 72 systems tested
   46 systems with Zr extraction between 10 - 83%
2. Ten stage shakeouts - 19 systems tested
   10 systems with statistically significant alphas
   5 systems with 94/91 alpha >1.006 (maximum 1.0084)
3. Column tests - 15 tests completed
   5 - Packed Column
   4 - Karr Column
   4 - Sparged Column
   2 - Jet Spray Column

94/91 alphas to 1.036

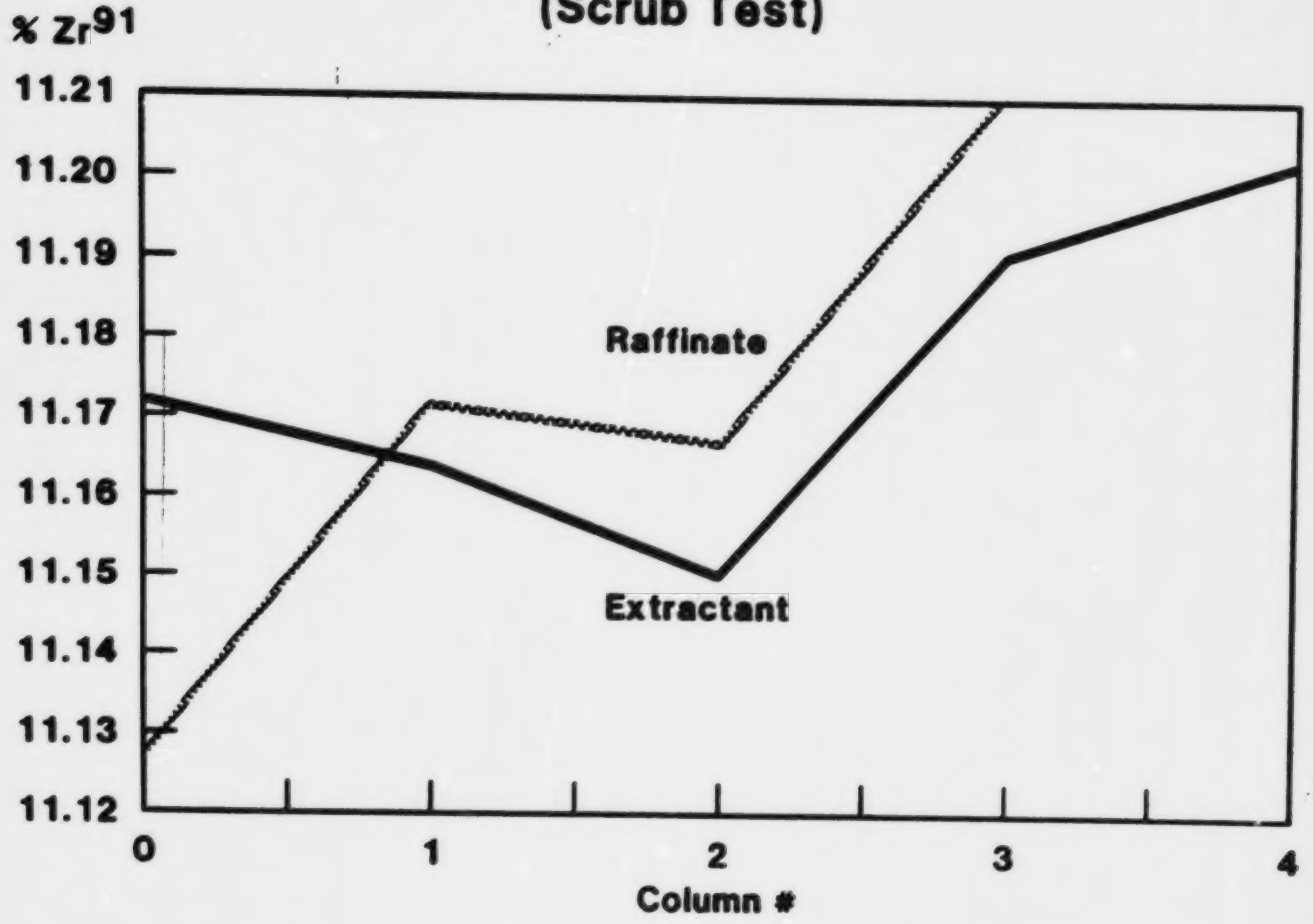
$ZrOCl_2$ IN AMINE EXTRACTANT

(Scrub Test)



ZrOCl2 IN AMINE EXTRACTANT

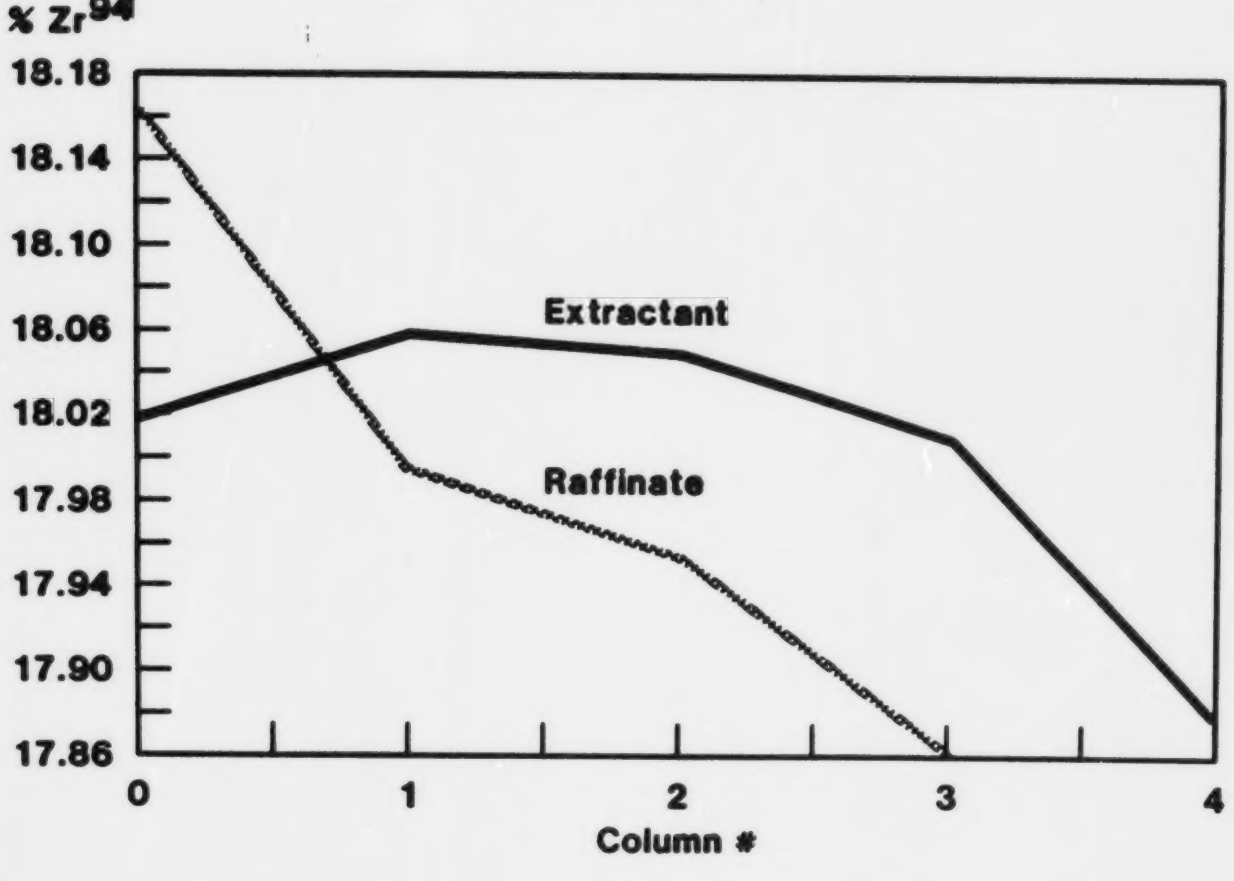
(Scrub Test)



88-99

$ZrOCl_2$ IN AMINE EXTRACTANT

(Scrub Test)



ECONOMIC ANALYSIS OF ZIRCONIUM ISOTOPE SEPARATION UTILIZING SOLVENT EXTRACTION

	Assumption
Capacity (Enriched Zr/Year; 000's lbs/yr)	900.
Plant Conversion Factor	.67
Value of Product ($/lb)	70.
Installation Multiplier	2.
Process Scale Factor	.70
OA/ Ratio	1.00
Electrical Costs ($/kwh)	.05
Maintenance (% of Installed Capital)	5.
Labor Cost ($/hr @ 10/Shift; 4 Shifts/Day	20.
Ammonium Bicarbonate ($/lb)	.23
Zirconium Tetrachloride (HF Removed; $/lb)	1.60
Tails Credit ($/lb of ZrO2	.25
Number of Stages	1250.

ECONOMIC ANALYSIS OF ZIRCONIUM ISOTOPE SEPARATION UTILIZING SOLVENT EXTRACTION

Ratio of Product to Feed	0.23
Estimated Pilot Plant Cost ($ in 000,000)	4.
Installed Capital Cost ($ in 000,000)	13.
Annual Costs ($ in 000,000)	
$ZrCl_4$	16.21
Ammonium Bicarbonate	.51
Power	.49
Maintenance	.65
Labor	1.66
Tails Credit	-1.03
Total Annual Cost	18.50
Incremental Cost/lb of Final TREX Product	30.00

CONCLUSIONS

- Zr isotope separation utilizing solvent extraction is technically feasible

- Approximately 1,250 theoretical stages are required

- Final product costs of $23 to $35 per pound of enriched Zr^{92}, Zr^{94} and Zr^{96} are likely with capital costs between $15 and $30 million for a 950,000 lb./yr. of ZrCly plant

PROGRESS OF WATERLOO EXPERIMENTS ON CO_2 MPD OF ORGANOZIRCONIUM COMPOUNDS

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Centre for Molecular Beams & Laser Chemistry
Waterloo, Ontario N2L 3G1

(Summary by H.D. Morrison, Ontario Hydro Research Division)

We are investigating the separation of ^{91}Zr by collisionless infrared multiphoton dissociation (IRMPD) of organozirconium molecules. Two groups are involved: Carty's group performs the synthesis, and Gough and Barnes perform the photolysis. Most molecules don't work. They either fall apart or explode or burn when we try to use them in our molecular beam machine. One molecule that is stable, and is accessible by CO_2 laser, is Zr-butoxide.

The molecular beam machine consists, in part, of a pulsed valve and a conical skimmer, with vacuum produced by a small diffusion pump. The CO_2 laser beam counterpropagates the molecular beam, thereby accessing all the molecules. A variable delay on the IR pulse yields kinetics information on the dissociation. Electron impact or an ArF excimer laser ionizes the dissociation products for diagnosis in a quadrupole mass spectrometer. This analysis works very well, especially with the ArF laser.

This work demonstrates poor prospects for commercial application of IRMPD of organozirconium molecules. The compounds are still difficult to handle and their vapour pressures lie well below 10 torr, the pressure where IRMPD would begin to be economic.

LASER ISOTOPE SEPARATION OF ZIRCONIUM - SO WHAT?

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I Overview

We were informed of renewed, industrial interest in zirconium-91 depletion, following the August 1983 incident at Pickering Unit 2, during informal discussions with Hydro staff in January 1984. Following these discussions we initiated a program of research into isotope separation of zirconium via the Atomic Vapour Laser Isotope Separation (AVLIS) process. Our reasons for investigating AVLIS were summarized in a presentation to the 1st Zirconium Isotope Separation Workshop (Ontario Hydro Report No. 84-306-K, 1984). These factors were:

(1) Nature has been kind to us: The industrial demand goal is to remove zirconium-91 from natural zirconium. Zirconium is element 40, hence it has an even number of PROTONS. Zirconium-91 is the only naturally occurring zirconium isotope with an odd number of neutrons. All even-even isotopes have zero nuclear spin. Hence zirconium-91 is the only isotope which will have nuclear spin and the only isotope to have hyperfine structure in its atomic spectrum. Zirconium lies in the middle of the periodic table, here isotope shifts are vanishingly small. Thus, the expected structure for zirconium atomic absorption lines involves a central clump due to all isotopes with lines due to zirconium-91 removed from this as a consequence of hyperfine structure. Thus, selective excitation of zirconium-91 was a reasonable expectation.

(2) AVLIS is an established isotope separation method for heavy metals: AVLIS is short listed by the United States Department of Energy as a viable candidate for the second generation US uranium enrichment plants. Pilot plants for AVLIS of uranium involving over 10 kW installed laser power are currently under construction at Lawrence Livermore National Laboratories (J.L. Emmett, W.F. Krupke and J.I. Davis, IEEE J. Quantum Electronics, QE-20 (1984) 591).

(3) Zirconium AVLIS parallels Uranium AVLIS: Both elements are refractory, reactive metals. Both elements have resonance atomic transitions in the range of red dye lasers. Both elements have ionization potentials in the range of 7 eV.

Accordingly, we began a program investigating zirconium AVLIS. The goals of the program were to investigate the spectroscopy of atomic zirconium vapour and to demonstration isotopically selective ionization of zirconium. To meet these goals we investigated three sources of atomic vapour. They were:

1. Hollow cathode discharges.
2. Volatile organozirconium compounds.
3. Laser vaporization of zirconium metal.

All three sources had individual merit and yielded results of importance to the project.

However, one, laser vaporization of zirconium metal, was so convenient, in a laboratory setting, that it enabled us to achieve all the initial program goals. This work has been summarized in two papers:

1. A high resolution laser induced fluorescence study of a supersonic Zirconium atom beam.

   O.L. Bourne, M.R. Humphries, S.A. Mitchell and P.A. Hackett

   Optics Communications, 56 (1986) 403.

2.Laser Isotope Separation of Zirconium Atoms Cooled in a Supersonic Beam

   M.R. Humphries, O.L. Bourne and P.A. Hackett

   Chemical Physics Letters 118 (1985) 134.

A further four papers dealing with subsidiary objectives are in preparation. Readers are referred to the papers above for detailed description of experimental procedures but the most relevant results are summarized below.

(1) Nature is indeed kind: The hyperfine structure of the first resonance transition $(4d^2 5s^2)a^3F_2 \rightarrow (4d^2 5s5p)z^3F_2$ at 613.6 nm was measured. Hyperfine shifts of up to 1200 MHz were observed for zirconium-91 lines. Furthermore, the isotope shift was only of the order of 100 MHz/amu. The hyperfine splitting in the upper state, as measured by quantum beat spectroscopy (see following paper), was small (20 MHz).

(2) Selective Ionization of all five zirconium isotopes has been demonstrated: Initial excitation of the 613.6 nm resonance followed by excitation with 308 nm photons (XeCl laser), absorbed in a **resonant** manner, gives efficient ionization.

Tuning the red photon gives selective ionization for all isotopes. Precise wavelengths for each isotope and the minimum measured selectivities are given below:

Isotope	Wavelength	Selectivity
Zr-90	613.6241 nm	> 100
Zr-91	613.6231 nm	> 100
Zr-92	613.6244 nm	> 100
Zr-94	613.6247 nm	> 100
Zr-96	613.6249 nm	> 100

The maximum selectivity measurable with our apparatus (a consequence of signal to noise considerations in our time-of-flight mass spectrometer) was 100.

(3) Laser Vaporization of zirconium metal provides a convenient source for spectroscopic and reactive chemical studies: We believe this to be self evident from the results presented above. Results to be published on precise values of the ionization potential of

free zirconium atoms, spectroscopy and isotope separation in the zirconium oxide (ZrO) molecule and the first observation of the zirconium fluoride (ZrF) molecule will reinforce this view.

These results and observations were presented to senior research personnel of qualified Canadian companies (AECL, CRNL and Ontario Hydro, Science Section) in March 1985. At that time we expressed our view that our results established the scientific feasibility of the zirconium AVLIS process. We expressed our view that the commercial viability of the process should be assessed and that such assessment should have strong input from all interested parties. We expressed and continue to express our willingness to collaborate in assessments of the viability of zirconium AVLIS, both through scientific input and through utilization of our in-house research program to provide necessary, further, parametric analysis of the problem. As yet we have made no formal inputs to such assessment processes.

II Where do we go from here?

We believe we have established the scientific feasibility of zirconium AVLIS. We will continue to carry out experiments to put limits on this feasibility. Questions such as: What are the values of cross-sections; What is the precise I.P.; Are there autoionizing states in the ionization continuum; and, could some of the required frequencies be provided from radiation sources other than lasers, remain of interest.

The question of the commercial viability of the process requires a strong commitment from parties interested in zirconium isotope separation in general and to zirconium AVLIS in particular. In the absence of such commitment time, and perhaps a window of opportunity, will be lost.

The techniques developed in this program are appropriate to and will be applied to isotope separation of many other elements. Of particular interest are radiopharmaceuticals (either in the production or purification of cyclotron spallation targets). This is because these elements can be no more difficult to separate than zirconium whilst the anticipated scale of production (mg/a-kg/a) would be far easier to achieve today than that for zirconium (100's Mg/a). These techniques are also applicable to the production of ultrapure elements and applications in areas of solid state physics have been brought to our attention. There are also many attractive features of the source we have described which make it highly suited to the preparation and characterization of new reactive, refractory chemical species and these studies will continue.

III Conclusions

We believe that our experience with zirconium AVLIS nicely illustrates several aspects of scientific problem solving. Within 18 months of hearing of the problem and in consultation with interested parties, we were able to identify a research direction, reallocate resources to the problem, find a solution and publish our findings. We trust that this momentum will be maintained.

MODELLING STUDIES OF ZIRCONIUM ISOTOPE SEPARATION VIA THE AVLIS PROCESS

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There have been relatively few measurements of fine structure of zirconium transitions. Isotope shifts have been previously reported and some hyperfine splittings have been observed. However, there is little information available for transitions originating on the ground electronic term. It is precisely these transitions which are of significance for isotope separation. In this paper we will briefly report upon techniques designed to investigate such structure in atomic zirconium transitions. However, the reader is strongly recommended to consult two other publications for a more detailed description of this work.

Intermodulated optogalvanic spectroscopy (Figure 1) and atomic beam laser induced fluorescence (Figure 2) were used. A commercial hollow cathode lamp was used as the atom source for the optogalvanic investigations whilst an atomic beam originating from laser evaporation of zirconium metal followed by supersonic expansion provided the source for the fluorescence data. In both cases the excitation laser was a commercial ring dye laser (Spectra Physic 380 D) with an optional pulse amplifier chain (Figure 3). Our investigation was restricted to the region 570 nm to 620 nm using the efficient and stable R6G dye and also because the necessary technology to generate high average powers in this wavelength range is well advanced. Figure 4 shows the doppler limited optogalvanic spectrum of the transition $(4d^2 5s^2)a^3F_4 \rightarrow (4d^2 5s5p)z^3F^0_4$ at 612.914 nm. It indicates that the spectrum consists of two general features, a central peak (even isotopes) superimposed upon a smaller but distinctive pedestal (hyperfine components of zirconium-91). Moreover the pedestal extends well beyond the Doppler limited width (1.3 GHz $\simeq$ 1240K) of the central maximum. This result is encouraging as it points to spectral components due to ^{91}Zr which are well removed from the even isotopes. Figure 5 shows the optogalvanic signal obtained for the same transition and 612.914 nm in the "Doppler-free" mode. This figure illustrates the even isotope structure at the central peak and the presence of at least one hyperfine component due to ^{91}Zr.

Figure 6 shows the Doppler free fluorescence spectrum of the transition $(4d^2 5s^2)a^3F_2 \rightarrow (4d^2 5s5p)z^3F_2{}^0$ at 613.24 nm. The spectrum shows four peaks which may be assigned to the even isotopes and four which may be assigned to ^{91}Zr. The linewidths of the even isotope peaks is measured to be 22 MHz which is greater than the natural linewidths (0.5 MHz) but of the order of the calculated Doppler broadening (9 MHz) and laser line width (7 MHz). The residual linewidth could be due to collision processes characterized by a "temperature" of 0.15 K. The width of the features assigned to the ^{91}Zr absorption are in general 1.5 times greater than those of the even isotopes. Moreover there appears to be a slight asymmetry to the red edge of the ^{90}Zr absorption. We have confirmed that the larger than expected width of the ^{91}Zr features are due to unresolvable hyperfine splitting of the upper level by performing quantum beat spectroscopy using the laser system of Figure 3 (the fluorescence decay for ^{90}Zr and ^{91}Zr are shown in Figure 7 and 8 respectively) and have concluded that the asymmetry of the ^{90}Zr peak is the result of the overlap between a ^{91}Zr peak and the ^{90}Zr peak.

We fully appreciate the fact that our molecular beam source may not represent a typical source for a large scale separation process. Therefore, we have developed a simple model which can generate the appropriate spectra for a "non ideal source". The two dominant spectral broadening mechanisms are Doppler (characterized by a temperature T) and the premature quenching of the excited state (characterized by a lifetime τ). Figure 9 shows typical spectra generated for the quoted values of T and τ, whilst Figure 10 shows a selectivity S defined as

$$\frac{[\text{absorption } ^{91}\text{Zr}] \,/\, [\text{absorption } (\text{Zr-}^{91}\text{Zr})]}{[^{91}\text{Zr}]_{\text{natural}} \,/\, [\text{Zr-}^{91}\text{Zr}]_{\text{natural}}}$$

for an assumed lifetime of τ=5 nsec. The latter figure demonstrates that even if T > 1000 K ^{91}Zr features can still be selectively excited.

FIGURE 1

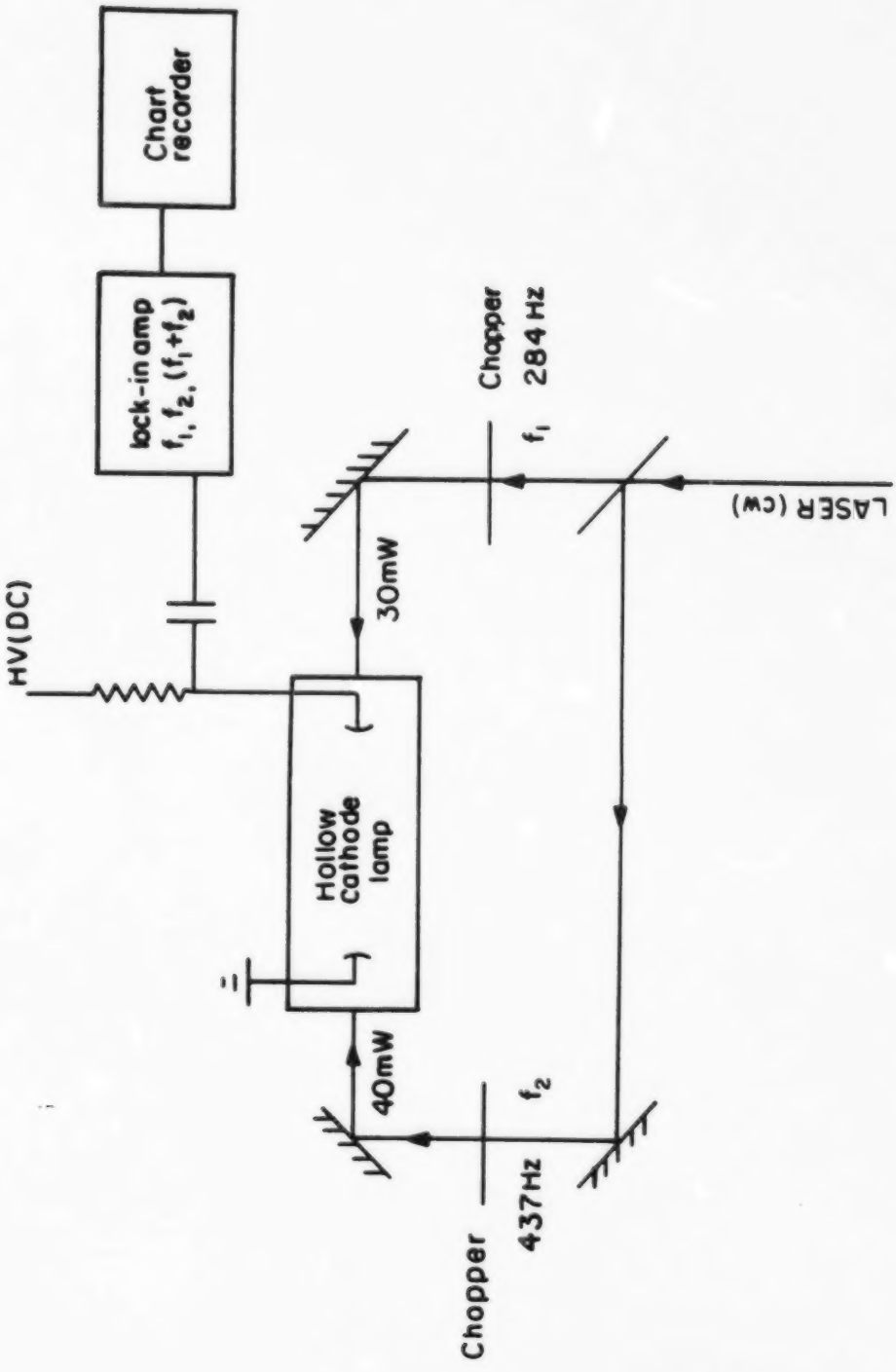
Chart recorder
lock-in amp $f_1, f_2, (f_1+f_2)$
Chopper
f_1 284 Hz
LASER (CW)
30mW
HV(DC)
Hollow cathode lamp
40mW
f_2
437Hz
Chopper

FIGURE 2

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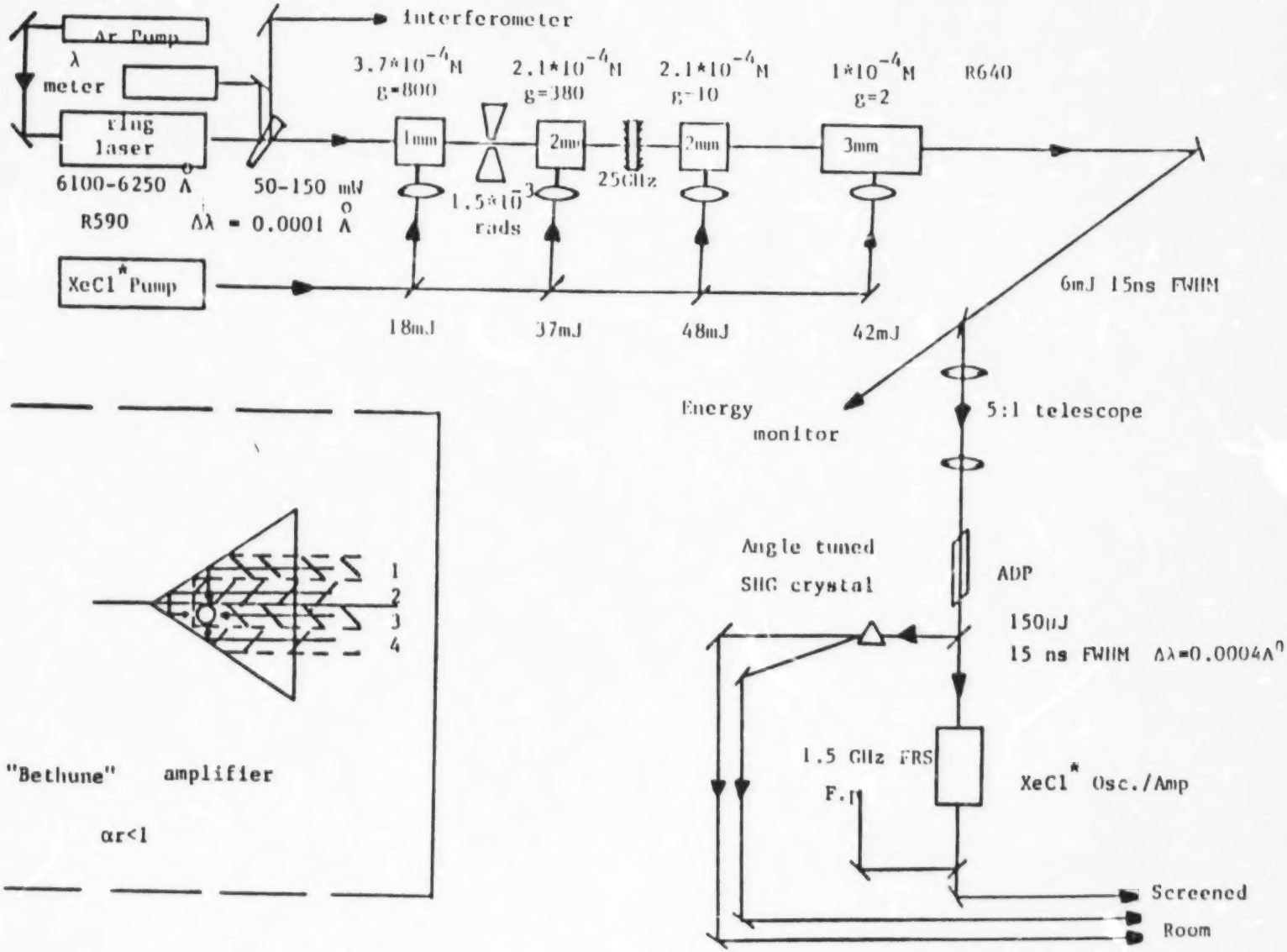

FIGURE 3

The amplifier chain

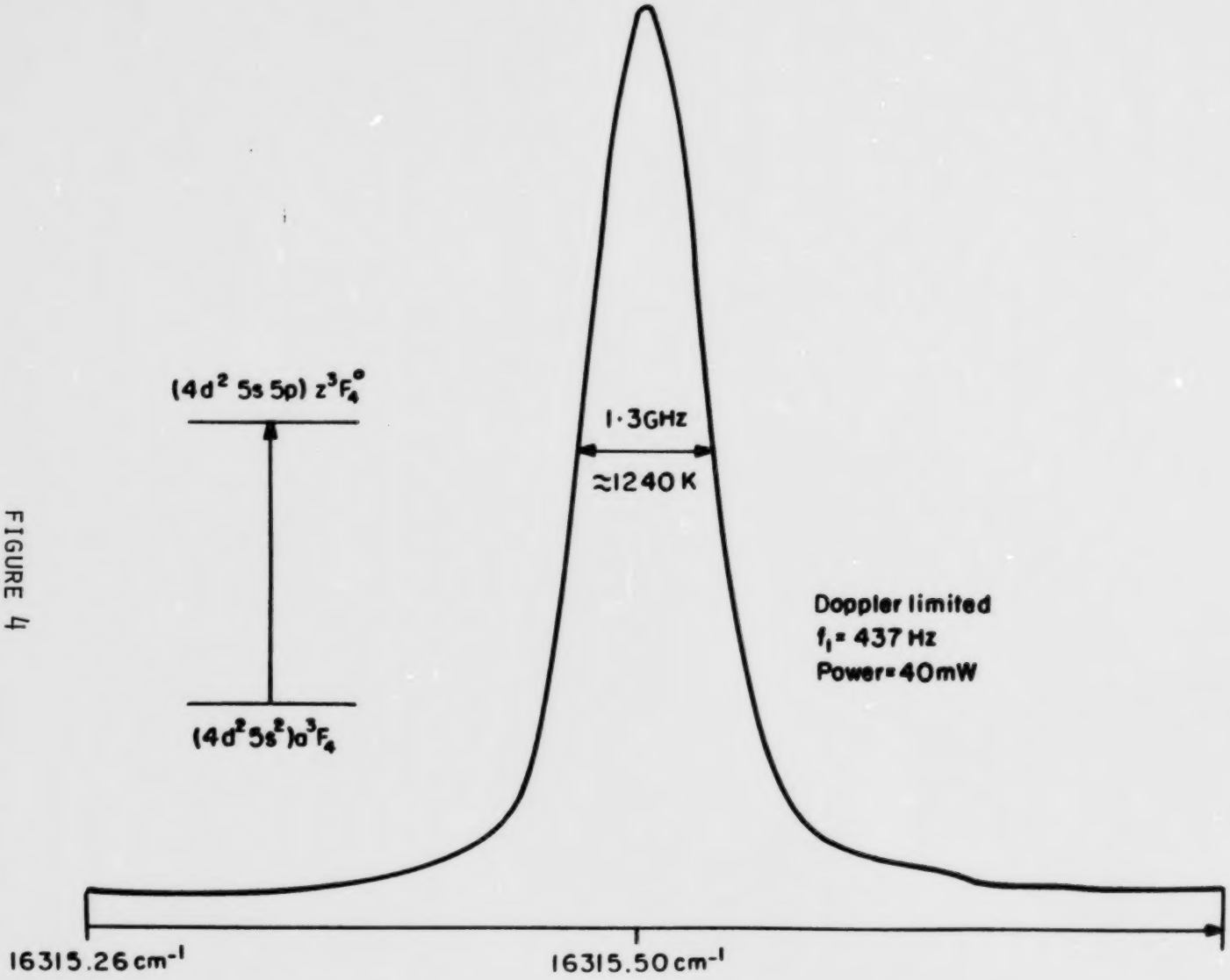
$(4d^2\,5s\,5p)\,z^3F_4^o$
$(4d^2\,5s^2)\,a^3F_4$
1·3GHz
≈1240 K
Doppler limited
f_1 = 437 Hz
Power = 40mW
16315.26 cm^{-1}
16315.50 cm^{-1}

FIGURE 4

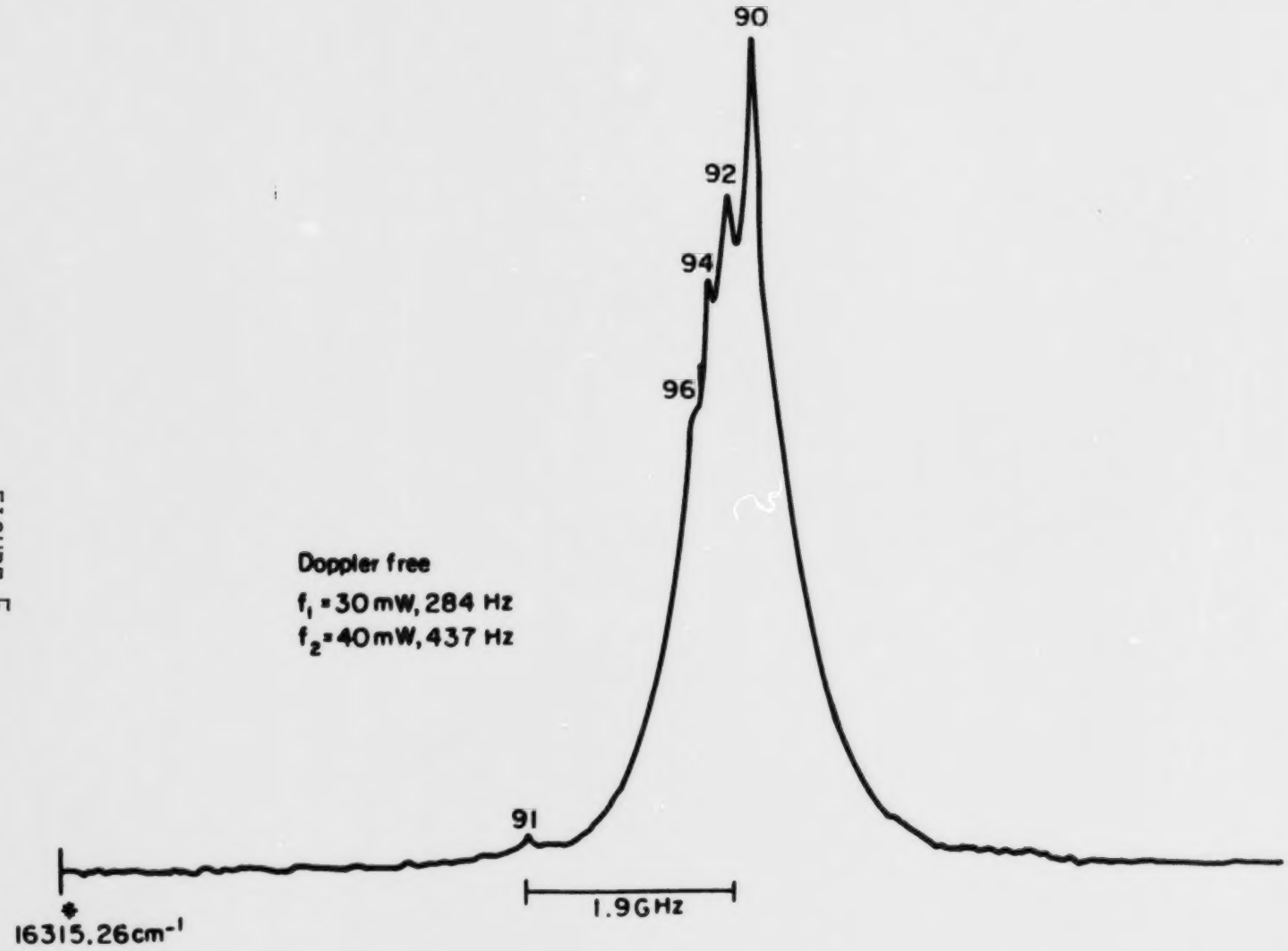
90
92
94
96
91
Doppler free
f_1 = 30 mW, 284 Hz
f_2 = 40 mW, 437 Hz
1.9 GHz
16315.26 cm^{-1}

FIGURE 5

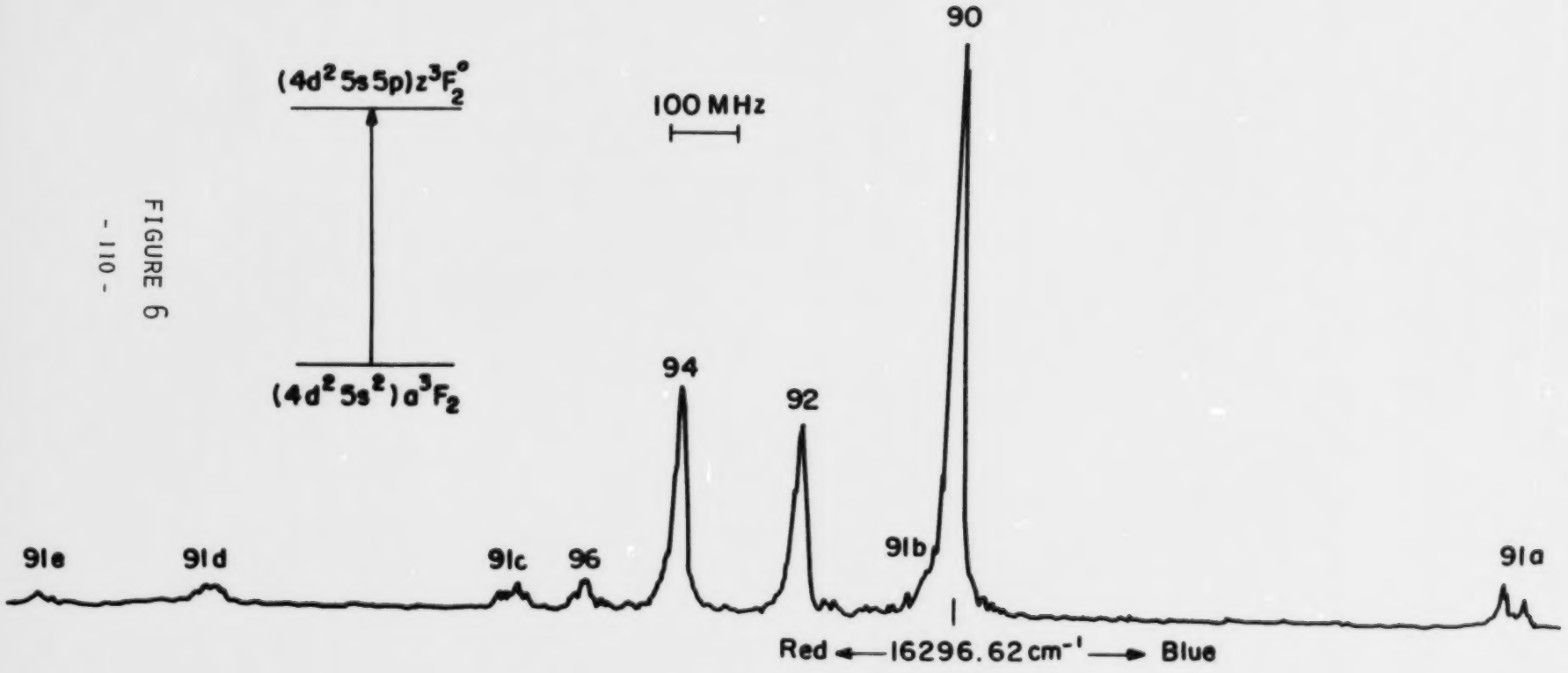

FIGURE 6

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FIGURE 7

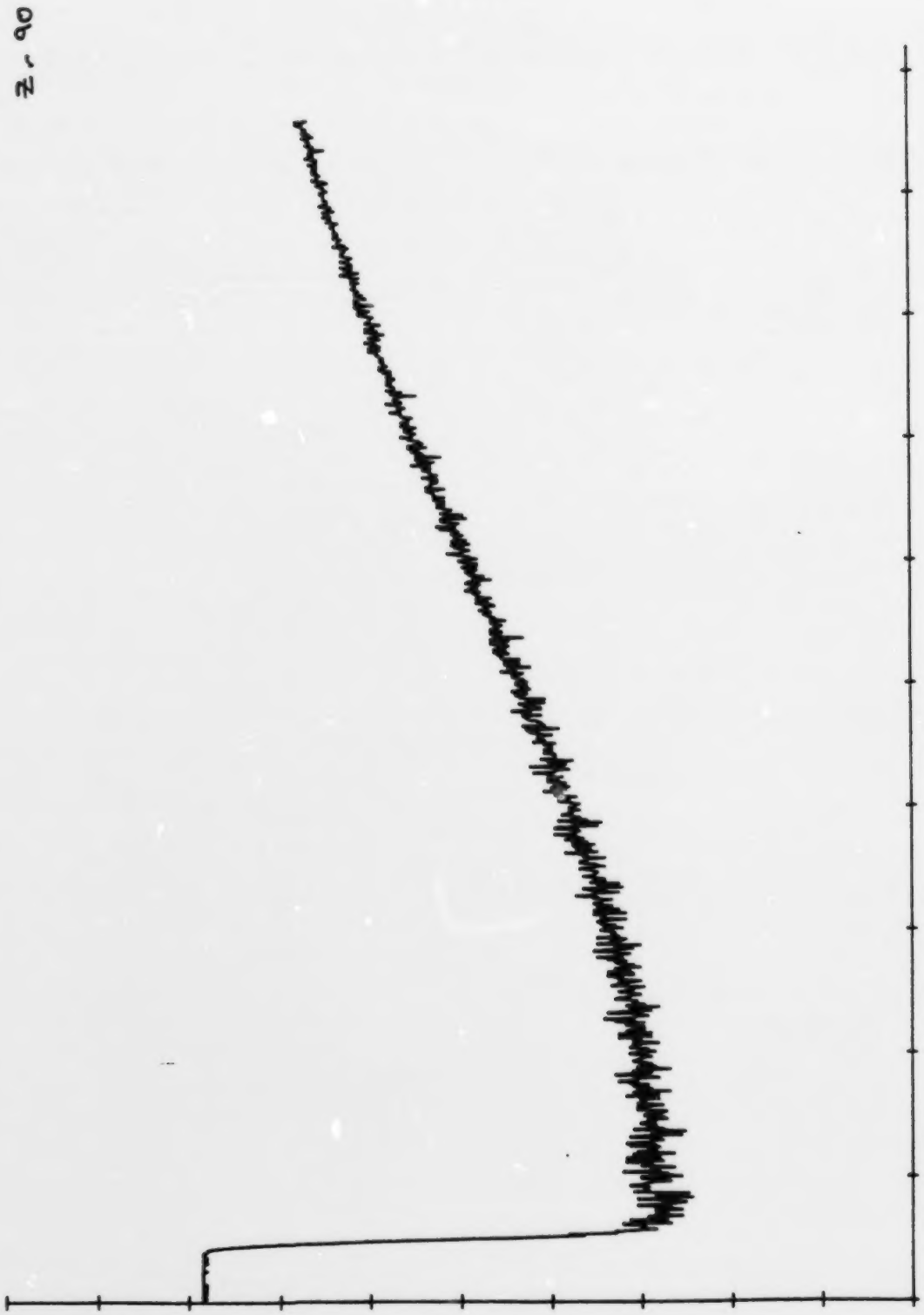

FIGURE 8

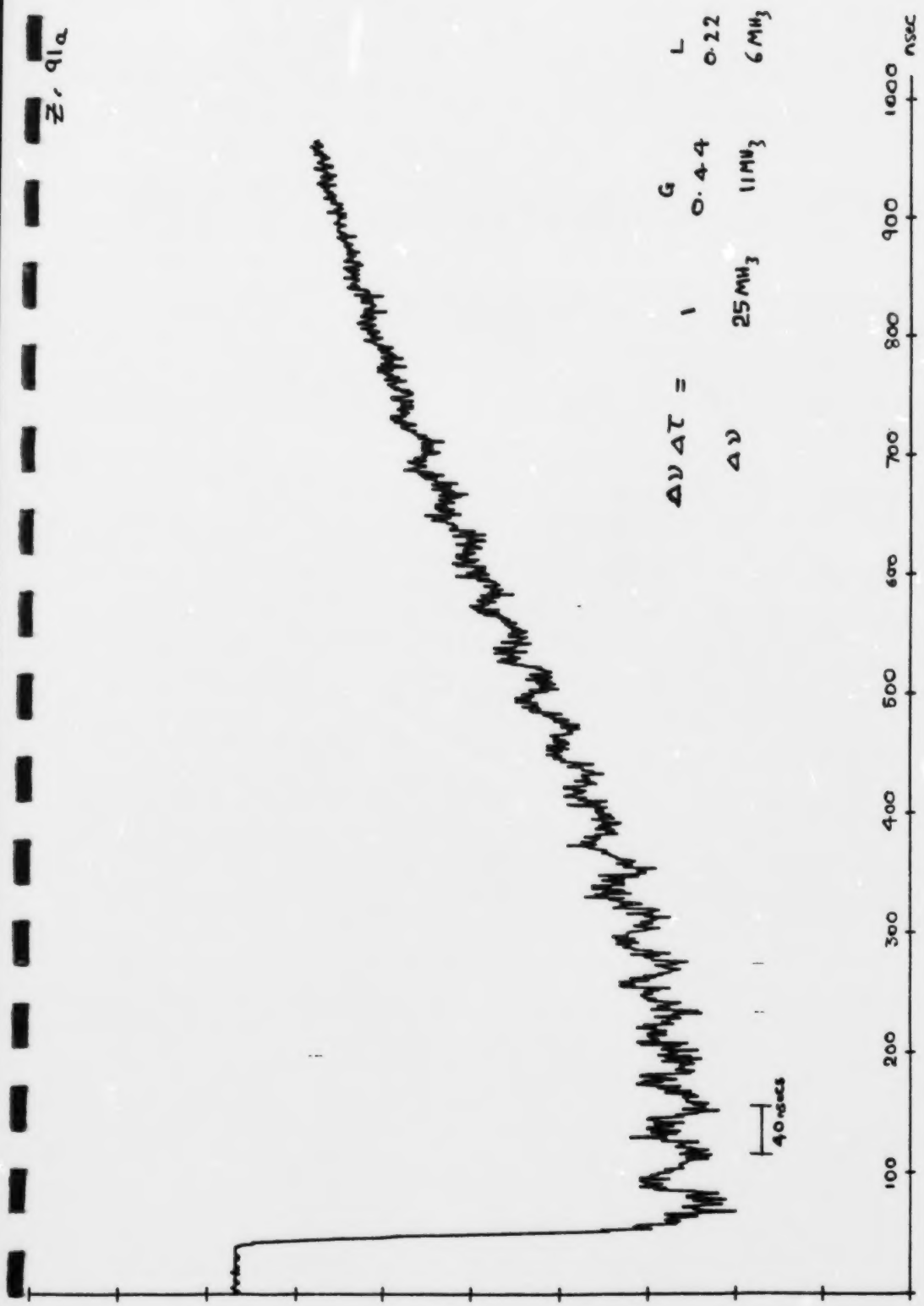

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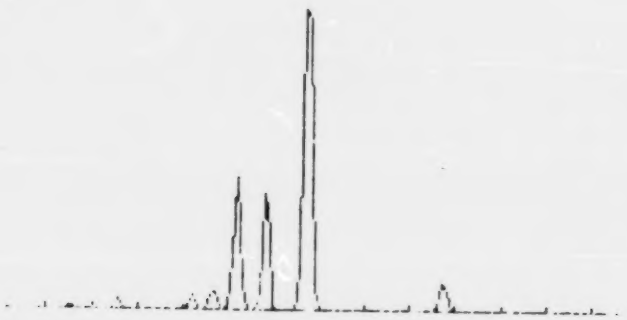
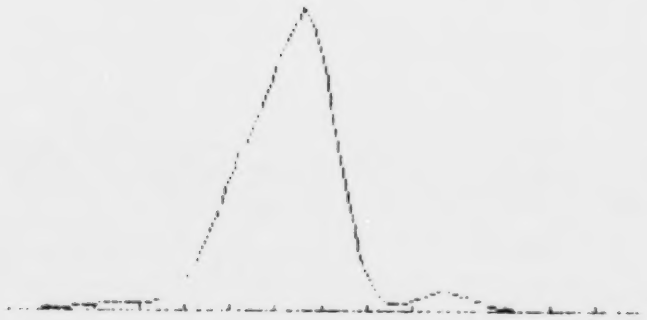
FIGURE 9



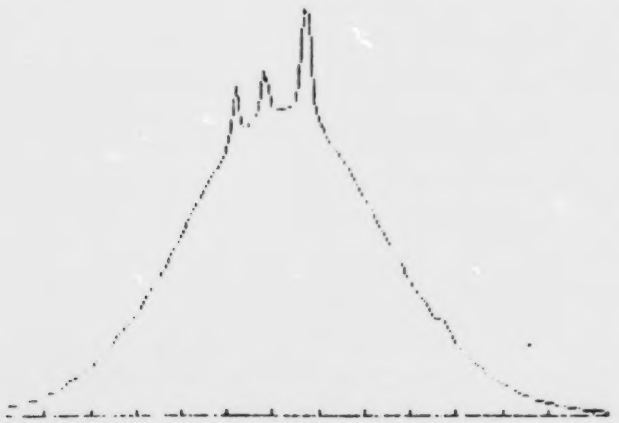
τ = 500ns

T = 1°k



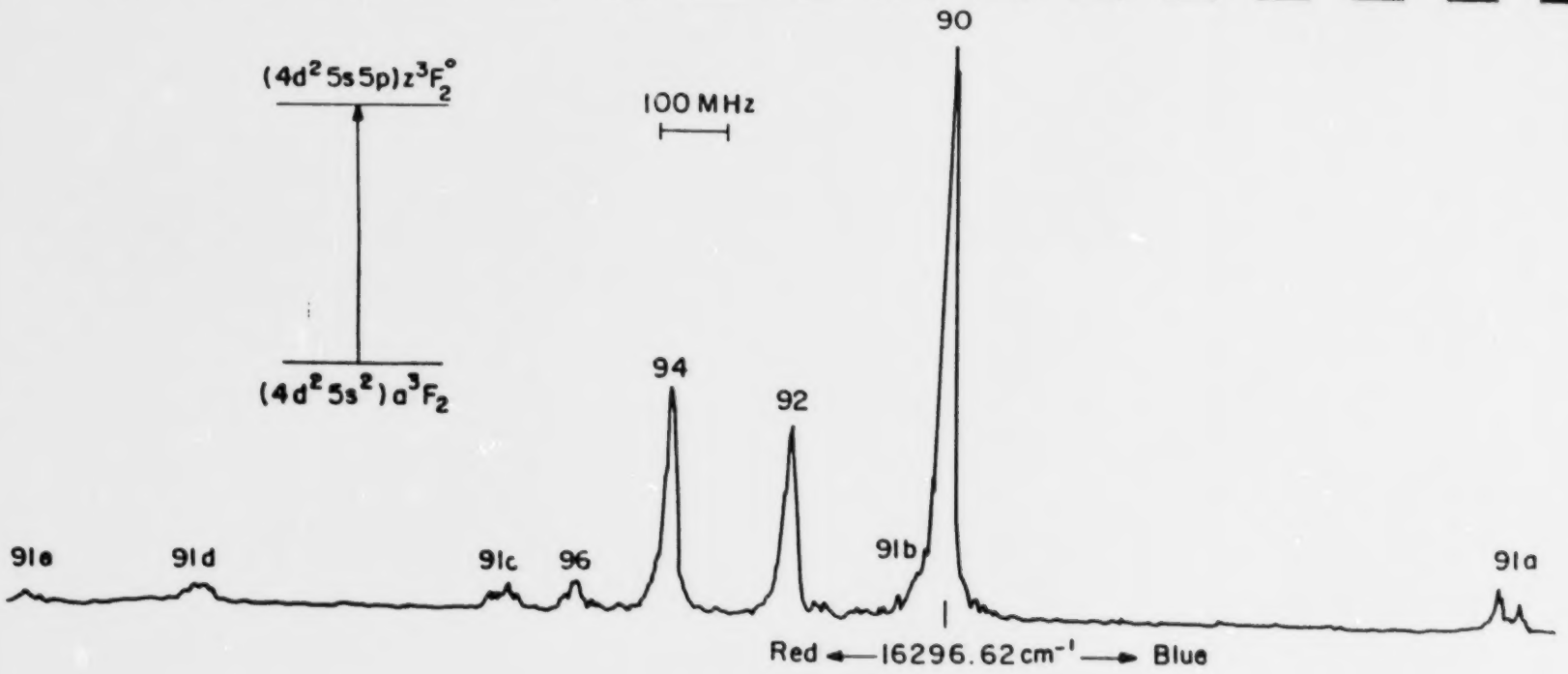
τ = 50nsecs

T = 100°k



τ = 5nsecs

T = 1000°k



525·4	554·7	4·0	0·8	100 K	2000·0
119·4	19·5	1·6	0·7	300 K	53·5
3·2·	2·0	1·0	0·7	1000 K	3·6
1·0	1·0	0·9	1·0	3000 K	1·7

$$S = \frac{\text{abs } Zr^{91}}{\text{abs } Zr - Zr^{91}} \Big/ \frac{[Zr^{91}]}{[Zr - Zr^{91}]}$$

our $\alpha = 180$

FIGURE 10

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COHERENT VACUUM ULTRAVIOLET PHOTOCHEMISTRY AND ISOTOPE SEPARATION

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(Summary by H.D. Morrison, Ontario Hydro Research Division)

The first requirement for doing vacuum ultraviolet (VUV) photochemistry is a source of intense VUV light, preferable a VUV laser, with emission above 6 eV (below 2000 Å). How do we make such a laser? The problem is that the radiative lifetime for VUV transitions is very short (varies inversely with the cube of the frequency), so that optical resonators are difficult to build. One solution is frequency shifting by nonlinear optics to use the second, third or even fourth harmonic of another laser. Second harmonic generation is very efficient, but you need crystals and they stop working below 2000 Å. Third harmonic generation is possible by 4-wave mixing in gases. This method retains the properties of the input beam and is very efficient in metal vapours. A conversion efficiency of 1% is available by mixing the output of two dye lasers in vapours of Sr, Mg, and Hg. The VUV output is coherent and tunable by tuning the frequency of one of the dye lasers. We have created a VUV probe by using Mg vapour at a pressure of 30 torr buffered with a rare gas to mix the output of two nitrogen laser-pumped dye lasers.

Our VUV probe produces lots of VUV between 1400 Å and 1700 Å. It is continuously tunable over a range of 3000 cm^{-1}. In demonstrations of fluorescence excitation spectra on CO_2 at 10^{-6} torr, we obtained an excellent signal to noise ratio in single shot recording. The VUV excitation generated very small quantities of decomposition product by single photon photolysis. The question is can it separate isotopes?

To separate ^{14}C we could work on CO_2 directly. Photolysis of $^{14}CO_2$ by one VUV photon yields ^{14}CO and O. In the presence of many such reactions the products become ^{14}CO and O_2, or the O atoms can be trapped to get pure ^{14}CO. Two points can be noted here: this reaction requires a VUV absorption, but are not all VUV absorption bands structureless? Fortunately there is some structure because there are Rydberg states, high lying excited levels, that show a pronounced isotope shift. For example, there is a 16 cm^{-1} shift between $^{12}CO_2$ and $^{13}CO_2$. Very high resolution spectra shows this shift clearly. In general, however, the spectra are hard to assign.